CONFORMATIONAL ANALYSIS OF SOME CYCLIC STRUCTURES

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Marie Ann Russell.

Chemistry Department

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ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

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Finally, but not least, I wish to thank my husband, Malcolm, without whom this thesis would have taken much longer to complete and who made the task less formidable than it might have been.

Marie Ann Russell.

To Mary and John Macdonald.

"The ordinary novel would trace the history of the diamond - but I say, "Diamond, what! This is carbon." And my diamond may be coal or soot and my theme is carbon."

D.H.Lawrence.

CONTENTS

SUMMARY

This thesis is composed of two parts: in the first the results from molecular mechanical calculations on cycloundecanes and cycloundecenes are recorded and discussed. In part two, x-ray diffraction analyses are reported for a series of eleven-membered ring structures and their conformations are correlated to the molecular mechanical results.

Molecular mechanics calculations are employed to locate the Global Minimum Energy Conformation (GMEC) of cycloundecane and those conformations within 20 kcal./mole of this GMEC. The results predict the existence of fourteen minimum energy conformations of cycloundecane - the first ten of which have strain energies differing by 3 kcal/mole or less. The GMEC, cycloundecane 1, is calculated to be only 0.49 kcal/mole lower in energy than the next conformer, cycloundecane 2. It is concluded that at room temperature cycloundecane is a mixture of several conformations.

The calculated low energy conformations of cycloundecane are compared with x-ray results and conformations predicted by other force field calculations. Comparisons are also made of cycloundecane 1 and 2 and the low energy conformations reported for cyclononane, cyclodecane and cyclododecane rings.

Introduction of a trans double bond into the cycloundecane conformations results in favourable changes in Baeyer, Pitzer and van der Waals strain. The predicted lowest energy cycloundecene conformer is observed experimentally in the crystal structure of dimethyl (8'-dimethylaminonaphthyl) ammonium dihydrogen tris(cycloundec-1-ene carboxylate) and bears a strong resemblance to the eleven-membered ring conformation observed in zerumbone 2,4 - dinitrophenylhydrazone. The results of the x-ray analyses of these compounds are recorded and discussed in the second part of this thesis.

Two new x-ray diffraction studies on cycloundecane derivatives are also introduced in part two. These are

cycloundecylmethyl 3,5 - dinitrobenzoate and cycloundecylmethyl - naphthylurethane. Both crystal structures exhibit disorder and it is concluded that the disorder arises from the presence of more than one conformation for the eleven-membered rings. Molecular mechanics calculations on the disordered rings result in model conformations with reasonable geometry and which correspond to cycloundecane 2.

PART I

MOLECULAR MECHANICS

CHAPTER ONE

BASIC PRINCIPLES OF MOLECULAR MECHANICS

1.0 INTRODUCTION

Stereochemistry is concerned with the three-dimensional shape of molecules and with how small differences in the three-dimensional structure may lead to differences in chemical reactivity. The first reference[1] to the concept of a tetrahedral carbon atom appeared in a note published in Palermo, Sicily in 1869 by E. Paterno but his discussion had no sequel and the rational explanation of optical activity must be credited to van't Hoff and Le Bel[2] in 1874. Van't Hoff continued to develop the rigorous and logical construction of classical stereochemistry but the importance of the relationship between the structure of a molecule and its reactivity was not generally appreciated until 1950 when D.H.R. Barton[3] published his pioneering work on conformational analysis, relating the chemical reactivity of steroids and polycyclic terpenoids to conformation. From that time, the development of various spectroscopic and diffraction methods to study molecules and crystals has provided a wealth of information on their structures and the influence of the spatial arrangement of atoms in a molecule upon its reactivity and its properties has been found to be of major importance. Experimental and theoretical methods capable of determining the detailed structure of molecules have become useful tools in stereochemistry.

The physical methods which have proved most valuable for winning accurate and detailed information about molecular structure all depend upon interactions between matter and radiation with, or without, energy change; energy may, or may not, pass between the radiation and the molecules. When there is a transfer of energy there is usually absorption or emission at specific wavelengths - these effects are studied by spectroscopic techniques e.g. NMR, IR, UV, ORD/CD. Spectroscopic measurements of frequency can be made with high accuracy thus related molecular parameters can also be determined with high accuracy.

When there is no transfer of energy between the radiation and the molecules there is elastic scattering of the radiation - the rays scattered from different molecules or from different parts of the same molecule will reinforce, or interfere with, one another: diffraction effects will occur. This principle can be applied even when the molecules are randomly orientated in the vapour state where electron diffraction enables the dimensions of simple molecules to be determined with considerable accuracy. The diffraction method comes to full fruition when the molecules are presented to the radiation in the regular array characteristic of the crystalline state.

Theoretical methods employed to elucidate structural information include Extended Huckel (EHT), Complete Neglect of Differential Overlap (CNDO), Modified Intermediate Neglect of Differential Overlap (MINDO), ab initio quantum mechanical and empirical force field (Molecular Mechanics) calculations. All these methods, with the exception of empirical force field calculations, are restrictive with respect to the computer time needed for the calculations. Molecular mechanics calculations do not impose impractical constraints on the computer resources and are capable of reproducing reasonable molecular geometries. Molecular mechanics calculations are, in essence, a computer based treatment of molecular models: atoms are represented as points in cartesian space and they interact according to some set of potentials which collectively are denoted as a force field. Force fields are described more fully in section 1.3 of this chapter. A molecular mechanics program consists of some means to input a molecular description and to output relevant molecular data. The energy computed is often referred to as strain or steric energy (V_s) and the program provides a means to vary the molecular geometry so as to minimise V_s. The success of this technique depends on the existence of a body of good experimental data for initial "parameterisation" of the force field. This term shall be explained in section 1.4 of the present chapter. Presently, reliable calculations can only be made for alkanes, alkenes, aldehydes, ketones, esters and peptides with up to fifty

atoms per molecule. There are many reviews on Molecular Mechanics calculations which are relevant to the present discussion[4-10].

1.1 CONFORMATIONS AND THE GLOBAL MINIMUM ENERGY CONFORMATION.

An important additional hypothesis ascribed to van't Hoff was the principle of free rotation around single bonds: he proposed that there was unrestricted rotation around a single bond resulting in an infinite number of stereoisomeric forms of a compound. Different arrangements of atoms that can be converted into one another by rotation about single bonds are termed conformations. However, from the early 1900's onwards, evidence rapidly accumulated[11-13] to indicate that rotation about single bonds was not free and that restricted rotation was very widespread.

Early work on enthalpy and entropy culminated in 1936 in the important suggestion by Kemp and Pitzer[14] that there is an energy barrier to rotation in ethane of ca. 3 kcal $mole^{-1}$ which indicates that rotation can be neither entirely free nor entirely hindered. At room temperature this small amount of energy is readily available to ethane molecules and the different conformations (or conformers) interconvert easily and cannot be separated from each other.

Not all of the conformers of a compound have the same energy. Where interconversion is easy we find that a molecule spends most of its time in the most stable or the lowest energy conformer i.e. the conformation with the absolute minimum of V_s which will be referred to as the global minimum energy conformation (GMEC).

The simplest molecules able to form various conformations are ethane and its substitution products. The barrier to free rotation of ca. 3 kcal $mole^{-1}$ around the central C-C bond seems to be occasioned by the fact that, as the methyl groups rotate with respect to each other, their hydrogen atoms become sequentially staggered and eclipsed. The potential energy (PE) of the molecule varies with the angle of rotation between two designated hydrogen atoms on adjacent carbons, as shown in Figure

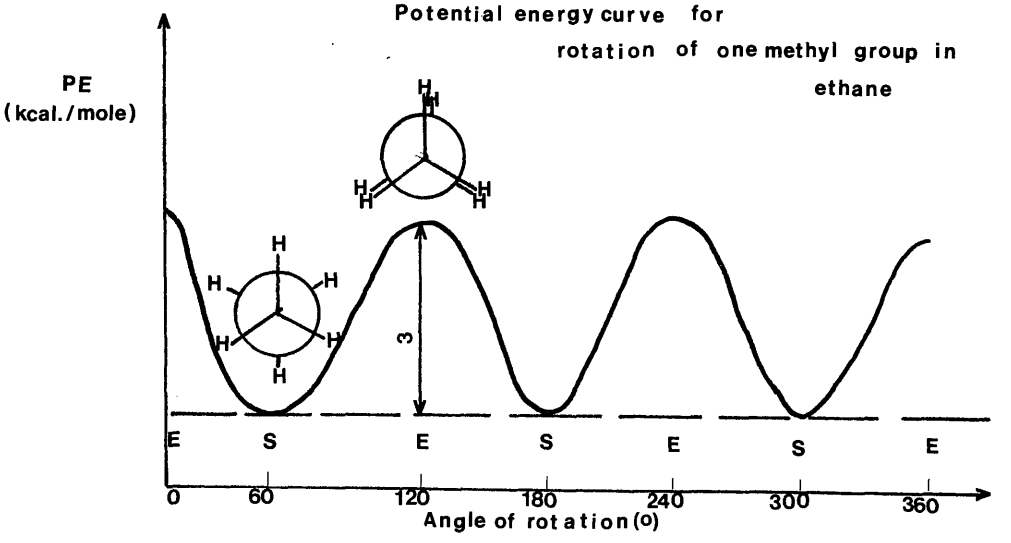
1.1 . The angle of rotation is defined more accurately as the torsion angle between two hydrogen atoms on neighbouring carbons. It has been established from vibrational spectra[15,16] that the minimum of PE coincides with the conformation in which the hydrogen atoms are alternately spaced when looking along the C-C axis - this (the GMEC of ethane) is called the staggered conformer and is repeated three times in a complete rotation around the central bond with the angle of rotation being 60^{o},180^{o} and 300^{o} for each minimum. Similarly there are three energy maxima (at 120^{o},240^{o} and 360^{o}) in which the hydrogen atoms on one carbon eclipse the hydrogen atoms on the other carbon as one looks along the C-C axis. These are termed the eclipsed conformers of ethane. Between these extremes of conformations there are an infinite number of possible conformations.

When two of the ethane hydrogens are replaced by other atoms or groups more complex energy curves arise. In 1,2 disubstituted ethane e.g. butane, the potential troughs and energy barriers are no longer equal - there are several different staggered conformations. There is an anti conformation in which the methyl groups are as far apart as they can be with a torsion angle of 180^{o} and there are two gauche conformations in which the methyl groups are only 60^{o} apart. It has been found that the anti conformation is more stable than the gauche[17-19] conformation by 0.8-0.9 kcal $mole^{-1}$: both are free of torsional strain but in the gauche conformation the methyl groups are crowded together and there is van der Waals repulsion between these methyl groups - the molecule is less stable as a result of this strain. The anti conformation, also referred to as the trans conformation , is the GMEC of butane.

Van der Waals strain can affect not only the relative stabilities of various staggered conformations but also the heights of the barriers between them. The energy maximum reached when the two methyl groups swing past each other is estimated[20,21] at greater than 4 kcal $mole^{-1}$. The situation is summarised in Figure 1.2.

FIG. 1.1

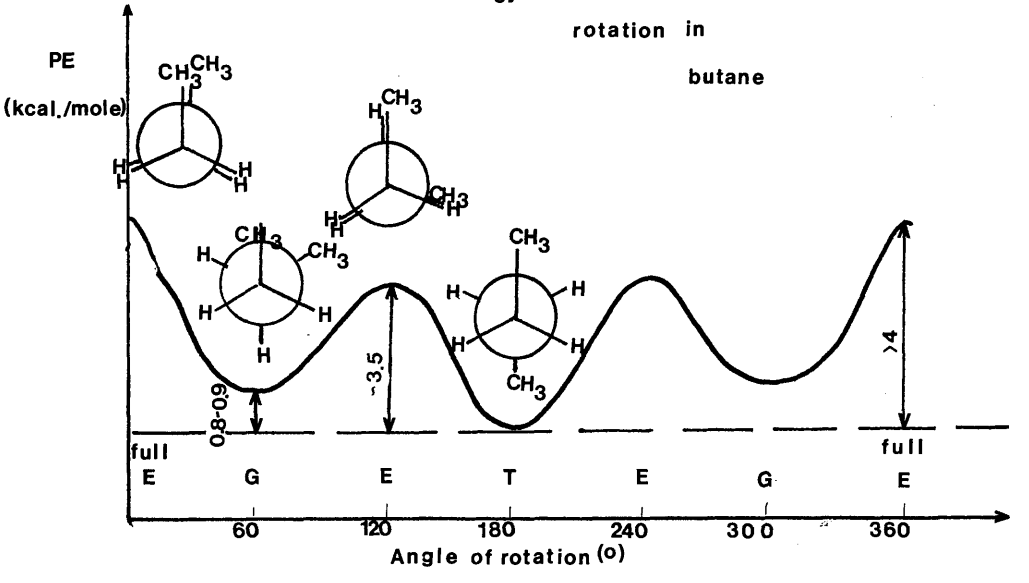
Potential energy curve for rotation of one methyl group in ethane



E – eclipsed
S – staggered

FIG. 1.2

Potential energy curve for rotation in butane



E – eclipsed
G – gauche
T – trans

Thus, there are several low energy conformations of butane separated from each other by energy barriers. Although the energy barrier to rotation in butane is a little higher than that of ethane, it is still low enough that - at room temperature, at least - interconversion of conformers is easy and rapid. Equilibrium exists and favours a higher population of the more stable anti conformer: the populations of the two gauche conformers are equal.

One finds that any compound is seldom a set of identical unchanging molecules - it is, rather, a mixture of conformations. If one conformation predominates, the physical properties of the compound will reflect this. If several conformations are well represented, the physical properties will reflect this. In order to understand the physical and chemical properties of a compound it is necessary, therefore, to estimate the lowest energy conformations and where applicable, the GMEC.

1.2 POTENTIAL FUNCTIONS

In molecular mechanics (MM) calculations a molecule is viewed as a system of particles held together by Newtonian forces. It is assumed that the molecule has a reference strain-free structure in which its bond lengths, valence angles and torsion angles possess optimal values. Deviations of the molecular geometry from this reference state result in unfavourable energy changes and the molecule is said to be "strained". All methods of MM express this molecular strain energy, V_s, as a sum of contributions from the arbitrary strain-free geometry.

The principal intramolecular interactions considered are bond length distortion, bond angle deformation, torsional interactions, non-bonded interactions and out-of-plane deformations. In the simplest treatments the six components are assumed to be independent of one another:

$$V_s = V_l + V_a + V_w + V_r + V_q + V_x \quad (1)$$

where V_l, V_a, V_w, V_r, V_q and V_x are the components of energy arising from bond length deformations, bond angle distortions (Baeyer strain), torsional (Pitzer) strain, non-bonded interactions, coulombic interactions and out-of-plane bending at trigonal atoms, respectively. Cross terms which account for coupling between the components are neglected here as they are usually very small and are only necessary if calculating vibrational frequencies very accurately. Such distinctions among types of deformation are artificial and purely a matter of convenience - the modes which are identified separately are manifested collectively as changes in energy by the molecule as a whole.

(a) BOND STRETCHING AND COMPRESSION.

Bond stretching and compression arises from the motion of bonded nuclei along the internuclear line. As seen in the analogous simple harmonic oscillator system of two masses connected by a spring, this vibration is governed by Hooke's quadratic law:

$$V_1 = \Sigma_1 \; 1/2 \; k_1 \; (1-1_0)^2 \quad (2)$$

where V_1 is the bond length deformation energy, k_1 is the bond stretching force constant, 1 is the observed bond length and 1_0 is the equilibrium bond length. The linear deformation of a single bond by as little as 0.03 Å requires the expenditure of 0.3 kcal $mole^{-1}$ and twice that for the stiffer double bond. Under normal circumstances very little bond stretching is encountered and this is a consequence of the very high values for k_1 (typically 200-1200 kcal $mole^{-1}$ $Å^{-2}$).

(b) BOND ANGLE BENDING.

Bond angle bending refers to the radial scissoring motion of the bond angle and this vibration is also governed by a Hooke's law relationship for small angular deformations (ca. 20°):

$$V_a = \Sigma_a \; 1/2 \; k_a \; (a-a_0)^2 \quad (3a)$$

where V_a is the bond angle deformation energy, k_a is the angle bending force constant, a is the observed valence angle and a_0 is the equilibrium valence angle.

For larger angular deformations the energy requirement per degree of angle bending progressively decreases as the angle is deformed more and more. To account for this anharmonicity in molecules it is necessary to introduce additional terms into the harmonic expression. The following equation is best suited to our model:

$$V_a = \Sigma_a \; 1/2 \; k_a \; (\Delta a^2 - k'_a \Delta a^3) \quad (3b)$$

where Δa is $(a - a_0)$ and k'_a is the anharmonic force constant.

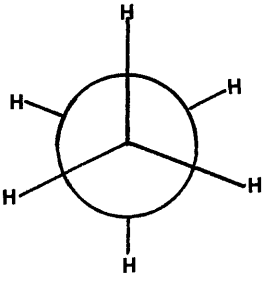
(c) TORSIONAL STRAIN.

Bond torsion refers to the rotational motion around the bond axis of adjacent carbons - strain arises from interactions between groups attached to the axial carbons. These are known as 1,2 interactions. The energy relationship resulting from variations of torsion angles from their most energetically favourable position may be written, in its simplest form, as:

$$V_w = \Sigma_w \; 1/2 \; k_w \; (1 + s\cos nw) \quad (4)$$

where V_w is the torsional strain energy, w is the observed torsion angle, n is the periodicity i.e. the number of times that a given conformation recurs in a complete revolution of 360°, k_w is the barrier to free rotation and s accounts for vector direction.

For instance,in ethane the staggered conformer shown below represents the situation of minimum torsional interaction (zero) and occurs three times during a 360° rotation.

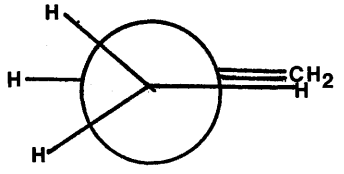


STAGGERED ETHANE

The threefold barrier is accounted for by setting n = 3 in

equation (4) and s = 1 i.e. the preferred conformation is staggered.

If an eclipsed conformation is the minimum as, for example, in propene then the threefold barrier about the C-C bond would have s = -1 and represents the situation shown below.

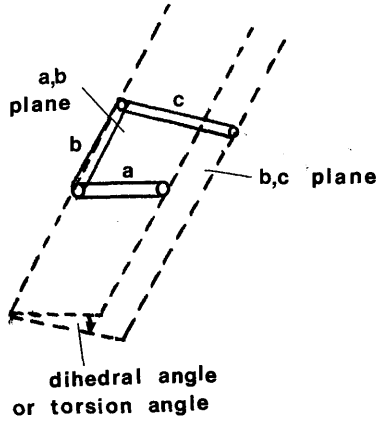


ECLIPSED PROPENE

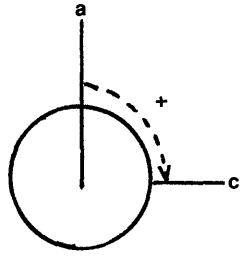
Expression (4) assumes that the barrier height is insensitive to the changes in the nature of the substituent and that each eclipsing interaction makes an equal contribution to the barrier. It has been found experimentally that energy barriers are dependent, to some extent, on the number of substituents but are reasonably insensitive to their nature.

Torsion angles and dihedral angles are two synonymous terms

commonly used to denote the angle which characterises the steric relationship between two vicinal bonds in a molecule. A system of three consecutive bonds a,b,c defines two half planes a,b and b,c intersecting along the central bond b. The perspective view is given below.



Perspective view



Newman projection

An alternative representation is given by the Newman projection. The angle made by the projections of the vicinal bonds in the plane perpendicular to the central bond, b, is the dihedral angle, or more appropriately, the torsion angle.

Despite the fact that the two expressions are often used interchangeably, the term torsion angle is preferable as it is more precise. It refers specifically to the dihedral angle made by three consecutive bonds, whereas there are many other types of dihedral angles which can be considered in a molecule. As indicated in the Newman projection, the angle is positive if the direction of rotation which superimposes the front bond onto the rear bond is clockwise, and negative if anticlockwise. The smaller of the two possible torsion angles defined by the system is usually chosen.

(d) NON-BONDED INTERACTIONS.

It is not always possible to account fully for the observed differences in the stability of conformers. However, there is little doubt that in the majority of instances (especially for hydrocarbons) the differences in stability arise to a large extent from differences in non-bonded interactions between neighbouring atoms. It would be a serious mistake to omit these interactions from the model.

Inter- and intramolecular non-bonded interactions are of great importance in stereochemistry: structure and reactivity depend to a large extent on this factor from which virtually all steric effects arise. Non-bonded interactions are the most difficult components of the steric energy to assign. They are the attractive and repulsive forces that exist between atoms or groups that are sufficiently close in space but not directly bonded to one another. The fact that gases condense to liquids and have compressibility factors less than unity at sufficiently low temperatures shows that there is attraction between molecules. At sufficiently close distances, however, gas molecules repel each other, as shown by the fact that the compressibility factor always increases with increasing pressure at sufficiently high pressures.

These intermolecular interactions may be represented by

plotting the potential energy, PE, of a pair of molecules as a function of their internuclear separation, r, as shown in Figure 1.3 . As the molecules approach each other PE decreases, due to mutual attraction, until a minimum is reached. As they approach still closer PE increases due to repulsion. The intermolecular force is given by the gradient of PE: for small separations ($r<3\mathring{A}$) the forces are repulsive and for larger separations ($r>4\mathring{A}$) they are attractive. There is an equilibrium (minimum energy) separation at r_o.

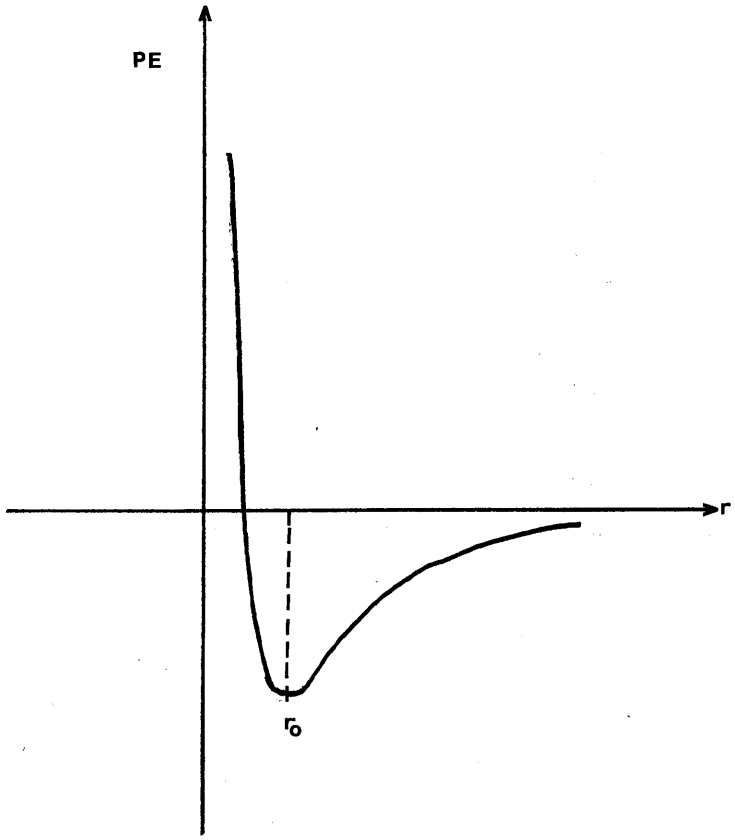


FIG. 1.3

For non-spherical units, PE is a function of the orientation of the two units[22,23] but it has so far proved impossible to determine the form of this term. For simplicity, the more straightforward treatment is retained here.

In order to produce the functional form of the non-bonded potential energy , V_r, it is necessary to have experimental data which can be readily interpreted. Such data are sparse and if they are available the many approximations needed to interpret them have resulted in numerous functions being proposed. The noble gases represent one case in which it has been possible to calculate the potential curve from a consideration of their deviations of behaviour from ideality. Normally, however, it is taken from interatomic or intermolecular potentials, a method which usually works well in practice despite its lacking a firm theoretical base[24].

The two most widely used types of intermolecular interaction potentials used are the Lennard-Jones potential (5a) and the Buckingham potential (5b):

$$V_r = \Sigma_r \ (Ar^{-n} - Br^{-6}) \quad (5a) \qquad n = 12 \text{ or } 9$$

$$V_r = \Sigma_r \ (A \exp\{-Br\} - Cr^{-6}) \quad (5b)$$

In both these equations the first term describes the short-range repulsive forces when the distance between the central atoms is less than the sum of their van der Waals radii. These are a result of a balance among nuclear repulsions, electronic kinetic energies, electronic repulsions and nuclear-electronic attractions. The $\{-(\text{constant})r^{-6}\}$ term accounts for attractive forces at larger r values which are referred to as London dispersion forces.

The precise form of the non-bonded interaction (5c) used in the present work[25] was derived by a least-squares fit of observed and calculated properties of crystalline hydrocarbons:

$$V_r = \sum_r E \ (-2a^{-6} + \exp[12(1-a)]) \quad (5c)$$

where α is a function of the distance coordinate alone and equals the van der Waals distance between the atoms (1 and 2) i.e. r, divided by the sum of their van der Waals radii, $r_1^* + r_2^*$: $\alpha = r/(r_1^*+r_2^*)$. E is a function of the energy coordinate which varies with the size of the atoms: for a pair of dissimilar atoms, E is often equated as the geometric mean of the E values for the two pairs of similar atoms.

The summation is over all pairs of non-bonded atoms three or more bonds apart, and although such a pairwise additive method sometimes produces incorrect results, by suitably careful "parameterisation" involving data at small internuclear separations, it is possible to obtain satisfactory representation. (These non-bonded functions are least reliable at these small distances as evidenced by the fact that the function (5c) has a spurious maximum at r = ca. 0.6 Å). Successful evaluation of such non-bonded parameters is essential for a good force field and there has been much discussion in the literature on this topic[5,26]. The evidence available suggests that the parameters for carbon and hydrogen utilised in the present force field give optimum results in most cases.

(e) COULOMBIC INTERACTIONS

A molecule which possesses polar groups has coulombic interactions between these groups. The potential energy derived from these interactions between charged atoms is given from classical electrostatics by:

$$V_q = \Sigma_q \, q_i q_j \, / \, D r_{ij} \quad (6)$$

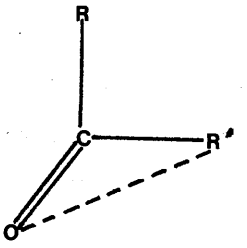
where V_q is the coulombic interaction energy, D is the dielectric constant between charged atoms i and j, q_i and q_j are the charges on these atoms and r_{ij} is the internuclear separation between them. Each atom, therefore, is treated as a monopole.

(f) OUT-OF-PLANE BENDING.

In their strain-free forms, groups attached to trigonal atoms e.g. olefinic and carbonyl atoms, should be planar. A deviation of the groups or of the trigonal atom from planarity results in a weakening of the pi bond. The potential energy stored in the molecule as a result of this deformation must be accounted for to ensure correct calculation of the geometry and energy of these types of molecules. This is equated via:

$$V_x = \Sigma_x \; 1/2 \; k_x \; (180-x)^2 \quad (7)$$

where V_x is the out-of-plane bending energy, k_x is the out-of-plane bending force constant and x is the improper torsion angle which is described below.



x, the improper torsion angle = R-C-O---R'

1.3 FORCE FIELDS.

All of the component potentials and their respective parameters are combined to form a force field (FF). The steric energy V_s is, therefore, a function of the geometrical parameters r, a, l, w and x which define the molecular conformation. Since the molecule seeks to achieve the level of lowest potential energy, the equilibrium value of these parameters are those corresponding to the minimum value of V_s. If the potential functions are known accurately the minimum of V_s may be computed and the values of the geometric parameters corresponding to this minimum of V_s may be estimated.

Today there are two main types of FF in operation - the Valence force field (VFF)[27] which is used here and the Urey-Bradley force field (UBFF)[28]. A major distinction between them is the treatment of the non-bonded interactions - the UBFF considers 1,3 and higher interactions explicitly whereas the VFF considers 1,4 and higher interactions. The VFF method, to a first approximation, relies on all the cross-terms being small whereas the UBFF approach requires no cross-terms. More sophisticated FFs[28-30] include bilinear cross-terms but, as mentioned previously, they appear to have more effect on calculated vibrational frequencies than on geometric or thermodynamic properties[9]. If one uses potential functions for non-bonded and coulombic interactions in a complementary fashion it has been found[31] that a separate function[32] for hydrogen bonding is not necessary.

There exists a third type of force field, the central FF, which assumes that molecules are held together by forces acting along lines between each pair of atoms. However, the central FFs are found to be less efficient than the VFF or the UBFF and are used rarely.

1.4 PARAMETERISATION OF FORCE FIELDS.

To calculate strain energies it is first necessary to have a set of strain-free structural parameters from which magnitudes of deformations are measured. This requires a large amount of experimental data on as wide a range of compounds as possible to be available in order to assign values for these structural parameters. It is advisable to limit the number of parameters as much as is possible to allow an understanding of the FF and to give it physical significance.

Trial values for stretching and bending force constants are derived from vibrational spectra while equilibrium bond lengths and angles come from microwave spectroscopy or diffraction (neutron, electron or x-ray) studies. The most crucial part of parameterisation is the choice of non-bonded potential functions: it is essential to include as much experimental data as is possible which exhibit this feature.

After estimating a set of force constants it is necessary to derive optimum values for FF parameters in relation to the experimental data. Two main methods are commonly used for such "parameterisation": (i) trial and error method and (ii) least squares method.

(i) Trial and error method.

Most of the FFs described in the literature involve FF components derived more or less by trial and error techniques. Starting values for these components are taken from various sources and are varied until the values giving the optimal agreement with experimental data are obtained.

(ii) Least squares method.

A least squares procedure for the systematic optimisation of potential constants was implemented by Lifson and Warshel[33] some time ago. Their procedure leads to the so-called "consistent" force fields (CFF) and operates thus: first, a set of reliable experimental data is collected from a large set of molecules which belong to a family of molecules of interest. All data used for the optimisation process are calculated and the differences between observed and calculated quantities evaluated. Subsequently the sum of the squares of these differences is minimised in an iterative process of varying the potential constants. The final values for these constants are the best ones possible within the data set and the analytical form of the chosen FF. The agreement with experimental data is reliable as seen by the CFF for alkanes and alkenes of Ermer and Lifson[30].

However, neither of these methods has a particular advantage over the other. Both are time consuming and method (i) provides equally good results[27].

1.5 POTENTIAL ENERGY MINIMISATION.

In general, the trial model for a molecular structure will not be the equilibrium structure since the initial coordinates of that molecule are only approximate e.g. if they have been derived from molecular models. To obtain information regarding the equilibrium properties of a molecule it is necessary to adopt an energy minimisation scheme, which will minimise the potential energy of the molecule in relation to its atomic coordinates, by systematically adjusting these coordinates until a minimum value is obtained. The numerous algorithms which exist for performing MM calculations may conveniently be divided into two categories; (1) those which make use of gradient information about the potential energy surface (steepest descent methods) and (2), those which make use of gradient and curvature information (Newton Raphson techniques). Both methods have relevant advantages and disadvantages in terms of memory requirements, computation time and the amount of information they provide. Various energy minimisation schemes are now considered.

(1) Steepest descent (SD) method.

Mathematically the problem is that of the location of function minima. At a potential energy minimum there must be no net force acting on any one atom i.e. a necessary requirement for an energy minimum is that the partial derivatives of the energy with respect to each coordinate equals zero i.e.

$$\delta V_s(x) \;/\; \delta x_i = 0 \quad i = 1,2....3N-6 \qquad (8)$$

since there are 3N-6 independent cartesian coordinates (coordinate vector, x) for an N atomic molecule.

To satisfy this system of equations, the derivatives are developed around a given starting value x_s (which must not be too far from the minimum) into a Taylor series truncated after the linear term. In matrix notation this is given by

$$\nabla V_s\ (x_s + \delta x) = \nabla V(x_s) + F_s \delta x = 0 \quad (9)$$

and

$$\delta x = -F_s^{-1}\, \nabla V(x_s) \quad (10)$$

where ∇V_s is the gradient of V_s and F is the matrix of second derivatives of V_s ($F_{ij} = \delta^2 V_s / \delta x_i \delta x_j$). F^{-1} is the inverse matrix of F. Substituting F in the latter equation by a diagonal matrix D with $D_{ii} = 1/L$ (L is a scaling constant) leads to the method of steepest descent:

$$\delta x_i = -L\ [\delta V_s(x)/\delta x_i\ ]x=x_s \quad (11)$$

One difficulty is finding a value for L i.e. there is a scaling problem.

One of the earlier approaches, pioneered by Wiberg[34] and extensively explored by Allinger[35-38] utilises this SD method. Each of of the 3N cartesian coordinates of a trial model is altered, in turn, by a small amount and the energy change is computed and stored. The coordinate is then returned to its original value and the calculation is repeated for the next coordinate. After the program has cycled over all the coordinates they are changed by an amount proportional to the energy change calculated for each and in the direction which lowers the energy. The process is repeated until the energy decreases less than a prespecified value (ca. 0.01 kcal $mole^{-1}$). It is hoped that the optimal geometry is achieved at this point. SD is an intuitively appealing method since it moves those atoms which affect the energy most adversely by the greatest amount. Furthermore, the procedure avoids getting "stuck" in saddle points of the potential energy surface and eventually succeeds in finding a minimum, though it may not be the lowest one[39]. Another disadvantage, apart from the scaling problem, is that some SD methods give maximisation or minimisation with equal facility. The criterion for a maximum rather than a minimum

depends on the starting position. The "pattern search" procedure used by Schleyer and others[4,5] may be regarded as an improvement on the simplest SD technique. The principal difference is that in a given cycle of the energy minimisation, the displacements calculated by a SD method are added to displacements from the previous cycle and the summed displacement is then applied. The effect is that if a particular atom is moving down a long shallow hill of the potential energy surface its motion is accelerated since the calculated corrections will be repeatedly in the same direction and the size of the correction term increases: the number of iterations required to approach the minimum will be less than for the simple SD method. An advantage of SD and similar methods is that the potential energy contributions of any analytical form can be easily accommodated. Another advantage is that potential energy minimisation proceeds rapidly if the molecule is relatively far from its optimal geometry - however, the process becomes progressively slower as the minimum energy geometry is approached and the optimal conformation is usually not reached as precisely as is required for the calculation of vibrational frequencies.

(2) Newton Raphson (NR) method.

A more highly developed method for locating the energy minima - developed independently by several groups: Jacob et al[28], Boyd[40] and Lifson and Warshel[41] - is the iterative minimisation based on the NR method. In equation (10), F is the matrix of second derivatives of V_s. By making different approximations to this matrix several techniques arise:

(i) Block diagonal (BD) method.

If $i,j \leqslant 3$ for each atom in equation (10) then F is a BD matrix[42,43]. Its use circumvents the scaling problem encountered in the SD method but it requires a more precisely defined trial structure. It is more effective, however, for bringing a crude, trial conformation into the vicinity of the

minima. The BD method correlates the movement of an atomic coordinate with other coordinates of the same atom.

(ii) Pure diagonal (PD) method.

The PD method utilises only the elements on the leading diagonal and sets all others to zero. This, in effect, treats the movement of each atomic coordinate in isolation from the rest of the molecule. It has recently been noted[10] that the PD method is more tolerant of the trial structures than the BD method.

(iii) Full matrix (FM) method.

In later stages of minimisation it is necessary to use a method which has better convergence properties than those previously mentioned: such a method is the NR technique which leaves all the terms of matrix F as they are originally. It requires a very good starting structure (in general, derivatives should be less than 0.05 kcal $mole^{-1}$ $Å^{-1}$) but converges very rapidly to give derivatives of the order of 10^{-7} to 10^{-8} kcal $mole^{-1}$ $Å^{-1}$. It is necessary to have a pre-optimised structure using, for example, PD or BD methods.

The matrix F is sixfold singular i.e. it has six zero eigenvalues corresponding to three rotations and three translations of the molecule, thus the set of equations (10) cannot be solved directly. The reciprocal of F can be determined by the generalised inverse method[33] which requires the diagonalisation of F or can be determined by the reduced F matrix technique[6]. The latter technique is deficient insofar as it fails to yield a generalised inverse that is unique and it is not used here. Methods of calculating a generalised inverse matrix are discussed more fully in mathematical text-books.

Since the FM method takes into account all the interatomic interactions it yields a very good representation of the symmetry

of a molecule; its excellent convergence properties result in better values for the geometrical parameters generally and for the torsion angles in particular. Torsion angles are significantly altered when the molecule departs even slightly from its minimum energy state. The energy, on the other hand, is not usually altered by a significant amount on moving from BD or PD methods to the FM method. A further advantage of the FM method is that it allows differentiation between maxima and minima on the potential energy hypersurface due to the inclusion of the second derivatives of V_s in the calculations.

No matter which method is employed to minimise the V_s it is necessary to calculate the first and often the second derivatives of V_s with respect to the coordinates. This uses 60–80% of the total computer time involved in the energy minimisation process thus, it is essential to consider carefully the method by which they are calculated. There are two basic options available[10]:

(a) Analytical calculation of the derivatives.

These are difficult to program and are best used with an established FF[11] where only production work is undertaken.

(b) Numerical calculation of the derivatives.

These are readily programmable and are more versatile analytical derivatives. This latter feature encourages the use of numerical derivatives when development of a FF is in progress.

To summarise: in general it is necessary to combine two minimisation procedures to achieve an optimal geometry of a structure. The present work uses a two stage Newton Raphson procedure combining full matrix minimisation with either block diagonal or pure diagonal methods: derivatives are calculated numerically.

1.6 LOCATING THE POTENTIAL ENERGY MINIMUM OF CYCLIC STRUCTURES.

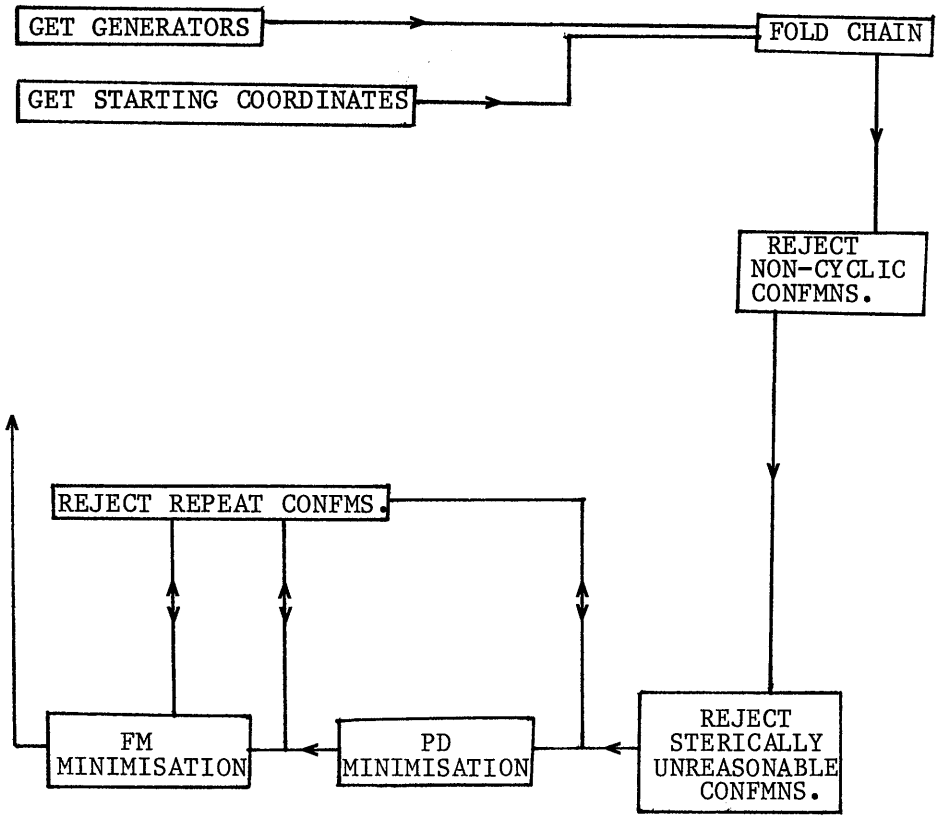
The examination of working models of ethane and butane readily affords all their possible conformations. If, however, one moves further along this homologous series of alkanes it soon becomes obvious that the number of possible conformations for each structure grows with increasing length of the carbon chain. Establishing the GMEC of any large open chain molecule would be an extremely arduous and indecisive process unless there are simplifying factors introduced into the calculation.

Efforts to make the location of GMECs more systematic have so far only been made for cyclic oligopeptides[44-46] and globular proteins[47-50]. The present work extends this to cyclic hydrocarbons. Factors limiting the number of possible conformations exist for all these classes of compounds: an important constraint on the possible conformations of any arbitrary chain of atoms is ring closure which has been fully employed in the algorithm used here[51].

This algorithm not only locates the GMEC of cyclic molecules but also enables discovery of all the low energy conformations of the cyclic structure concerned. It is not limited to a specific class of cyclic structures but is an almost automatic general computational procedure.

In addition to the routines specific for global energy minimisation there is available an advanced molecular modelling system, the Glasgow University Chemical Graphics System[52] (GUCGS), which provides a multitude of services e.g. examination of doubtful conformations generated by the GMEC algorithm and local minimisation of proposed conformations. Figure 1.4 introduces a block diagram of the full global minimisation procedure and the following paragraphs explain each step more fully.

FIG. 1.4 SUMMARY OF THE GLOBAL MINIMISATION PROCEDURE



The first step in the algorithm consists of obtaining the "generators". This term has variable definitions depending on which class of structure is being examined. For polypeptides it is used to denote the (Φ,Ψ) pairs[53] of torsion angles preferred by the amino acid residues constituting the polypeptide under consideration. These allowed torsion angles are estimated from Ramachandran maps [54] for each consecutive dipeptide pair present in that polypeptide. For cyclic alkanes the procedure is more straightforward. The higher normal hydrocarbons can be broken down into a series of n-butane systems. Each successive C-C bond of the chain will prefer the low energy conformational

arrangements of n-butane i.e. anti or gauche conformations. The generators for cyclic alkanes are simply the torsion angles evidenced in these low energy butane conformers i.e. 60°, -60°, 180°.

The coordinates describing an arbitrary arrangement of an open chain structure of the compound being investigated would normally be taken from x-ray crystallographic results of the structure concerned or would be built from the aforementioned GUCGS.

This chain would then be folded into a succession of probable low energy conformations corresponding to all possible combinations of generators.

A simple pattern search procedure which depends on geometric rather than energetic criteria to effect ring closure would then be tried on the folded chains: each ring torsion angle is allowed to vary by up to $\pm 20^{\circ}$ from its initial value in an attempt to close the ring within a prespecified end-to-end distance. Conformations which do not have an end-to-end distance within a maximum deviation from the target distance are rejected at this stage.

If these calculations are performed on an homopolymer, there is every possibility of repeat conformations being generated which are related to the original conformation by advancing the pattern of torsion angles by one or more stages. These repeat conformations are also rejected.

Each surviving conformation has its connectivity calculated on the basis of a maximum bonded distance and those with ten or more connections in excess of this predetermined distance are rejected due to the presence of very short non-bonded intramolecular contacts. This test is only applied to the main chain atoms as steric crowding of substituent atoms is usually resolved satisfactorily during the subsequent energy minimisation

calculations.

The final conformations should be capable of refinement by energy minimisation but can be individually examined via the GUCGS prior to minimisation, as a precaution.

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CHAPTER TWO

LOW-ENERGY CONFORMATIONS OF CYCLOUNDECANE AND ITS DERIVATIVES

2.0 FOREWORD.

The basic concept of conformational analysis is that certain chemical and physical properties of organic compounds are related to preferred conformations. It is important, therefore, to be able to determine the energy (or enthalpy) of a conformation. In general, the determination of the absolute energy is not possible and conformational analysis is restricted to comparisons of energy components for various conformations of a chemical species, or for the conformations of closely related species.

The most convenient parameters for the definition of the spatial arrangements of the atoms in a species are bond distances, bond angles and torsion angles, because they are independent of the coordinate system. For the purpose of conformational analysis, one considers the change in energy due to distortions of the bond lengths, bond angles and torsion angles from their most favourable values; this increase in energy content, usually called strain or steric energy and represented by V_s, is then calculated. Another important contributor to the V_s is the repulsive energy between non-bonded atoms i.e. non-bonded interactions, which is the most complex component of the V_s to be calculated. In spite of the difficulty in calculating V_s, conformational analysis has assumed the greatest importance for organic chemistry and it has been observed that several groups of compounds exhibit particularly stable conformations which change only slightly under further small strains. The classical example of such a conformation is the chair form of the cyclohexane skeleton and a profusion of such compounds is available in nature to which conformational analysis can be applied.

Semiquantitative conformational analysis has not been as successful for cyclopentane and cycloheptane; their various stable conformations are separated by energy barriers which are not as high as in the cyclohexane series[1] thus neither possesses a favoured conformation. This is observed in other members of

the homologous series. It was realised at a relatively early date that the special and often very marked, physical and chemical properties of medium-sized[2] ring compounds and in particular their comparatively high strain, were of a conformational origin: models of such compounds in which the three major components of strain (i.e. angle strain, torsional strain and non-bonded interactions) are simultaneously minimal, cannot be constructed[3]. Organic chemists could only conjecture how the total strain is distributed over the various strain components. They could do no more than speculate whether the medium-sized rings exist in one or more stable conformations, or whether they are to be regarded as relatively mobile particles with a large number of conformations almost equal in energy but differing in form[4]. Some important answers to these questions have been provided on the basis of information derived from spectroscopic[5] and x-ray diffraction[6] studies. With the advent of computers it has been possible to calculate the energy and detailed geometry of molecules of varying size by the method of molecular mechanics (MM) which can now be regarded as a practical research tool. The simple cycloalkanes $(CH_2)_n$ with n = 5 to 12, are compounds which have frequently been studied by force field calculations[7-12]. This preference results from their simple structures and from the abundant available experimental material (structural[13], thermochemical[14,15] and vibrational spectroscopic[5,16,17] data). There remains, however, a distinct shortage of available structural information for the eleven and higher odd-membered rings.

The present study attempts to predict <u>all</u> possible low-energy conformations of cycloundecane by application of the computational procedure described in Chapter One, namely, the White-Morrow algorithm[18-20] for location of the GMEC and other low-energy conformations. This algorithm has previously been used to locate all the low-energy conformations of cyclic tetrapeptides[18-20], and the present study is envisaged as an extension of the applicability of this algorithm.

Starting coordinates were obtained by construction of undecane via the GUCGS[21] described in the previous chapter. Torsion angle generators employed for elucidation of all the cycloundecane conformations were taken as $+60^{\circ}$,-60° and 180°.

A fundamental requirement for successful MM calculations is a force field which will reproduce sufficiently accurate geometries and energies. The force field used here is the White-Bovill Force Field[22] which has been thoroughly tested[19] in its application to acyclic and cyclic non-conjugated alkanes and alkenes. The parameters of this force field are recorded in the appendices.

2.1 INTRODUCTION TO MEDIUM-SIZED RING COMPOUNDS.

Although cycloalkanes form an homologous series, they also exhibit behaviour uncharacteristic of an homologous series: no smooth regular interdependence of physical and chemical properties on ring size is observed. Rather, a seemingly anomalous discontinuity is found for a wide range of physical and chemical properties of the medium rings[4] i.e. the eight- to eleven-membered ring systems - with a turning point at the ten-membered ring.

The excess combustion enthalpies of the cycloalkanes allow an estimate to be made of their total strain relative to their acyclic analogues which are assumed to be strain free[2]. Small, normal and medium rings tend towards high relative heats of combustion while the larger rings and cyclohexane exhibit "normal" heats of combustion similar to their acyclic counterparts. The estimated strain energies are detailed below:

RING SIZE (n):	5	6	7	8	9	10	11	12	13	14
TOTAL STRAIN : (estimated) kcal mole^{-1}	7	0	6	10	13	12	12	4	5	0

It is evident that the medium rings are unusual in that they have a higher V_s than the normal and large rings and must, therefore, possess special conformational properties which distinguish them from the normal and large rings. As suggested, three types of strain are anticipated in medium rings, namely, transannular, Pitzer and Baeyer strain.

Transannular strain arises from intramolecular overcrowding as a result of van der Waals compressions across the ring; Pitzer strain results from unfavourable torsional interactions between substituents on adjacent atoms; while Baeyer strain results from distortion of the bond angles from their strain free values.

Before turning to an examination of the derived

conformations of cycloundecane, it is necessary to define the concepts and symbols which will be used. As before, a conformation is defined by the bond lengths, bond angles and the torsion angles. Of these three parameters, the bond lengths are practically constant and the bond angles change only by small amounts which affect the spatial form to a relatively small degree, though they play a significant role in determining the strain. Thus the spatial form can be described by specification of the torsion angles (TA) alone[9].

Chapter One introduced the concept of gauche and anti torsional arrangements i.e. TA of 60° for the gauche form and 180° for the anti form. In many cases the exact TAs vary from these ideal values and the following nomenclature[23] in terms of approximate TAs ($^{\circ}$) has been proposed:

TA	DESIGNATION	SYMBOL
60 ± 30	+syn-clinal	+sc
-60 ± 30	-syn-clinal	-sc
$\pm 180 \pm 30$	$\pm$anti-periplanar	$\pm$ap
0 ± 30	$\pm$syn-periplanar	$\pm$sp
120 ± 30	+anti-clinal	+ac
-120 ± 30	-anti-clinal	-ac

Syn-periplanar is synonymous with eclipsed, syn-clinal with gauche and anti-periplanar with anti. In the medium-sized rings, low-energy conformations will contain mainly staggered conformations having sc and ap TAs.

Another convenient way of representing the conformation of a ring[6] skeleton besides the one based on the indication of all TAs of the ring bonds, is by looking at the two adjacent torsion angles to each member of a saturated carbon chain or ring. (The spatial environment of that member is characterised by the conformations of its nearest neighbours). Considering only

staggered sc and ap partial conformations results in four conformational types of chain or ring members, designated as types I to IV, as shown below.

TYPE	Adjacent partial confmns.
I	+sc,-sc or -sc,+sc
II	-sc,-sc or +sc,+sc
III	-sc,ap or +sc,ap
IV	ap,ap

The chair form of cyclohexane consists exclusively of the ring members of conformational type I. The medium rings however, have conformations which are composed of all four conformational types which explains the striking divergence in the behaviour of the medium-sized rings of different sizes.

An even simpler nomenclature has been introduced by Dale[24,25], the so-called "wedge" system, which is most applicable and valuable for rings with ten or more members where the TAs are not too far from gauche or anti values. Dale assigns "sides" and "corners" to a conformation for naming purposes. Any carbon with two adjacent ring TAs that are either (+)gauche,(+)gauche or (-)gauche,(-)gauche is a corner. A true C_2 axis passes through a corner atom and the external substituents can be classified as isoclinal and are not sterically hindered[9]. Non-corner carbons have one external substituent unhindered (equatorial-like) and one hindered (axial-like). The number of bonds between corners are placed in square brackets to describe the conformation. Dale suggests that odd-membered rings, in order to achieve the least possible deformations at the corners, exist as three- or five-cornered conformations, designated as triangular and

quinquangular,respectively.

2.2 GENERATED CONFORMATIONS.

Application of the aforementioned algorithm for GMEC location using the prespecified generators resulted in the linear starting chain being folded up in all possible permutations of the generator values. The resulting chains were subjected to a series of constraints and tests in order to identify and discard sterically unreasonable conformations. The remaining conformers were examined visually via the GUCGS and those with extremely bad non-bonded interactions arising from overlapping CH_2 groups were rejected.

All of the surviving conformations were optimised using the two stage Newton-Raphson energy minimisation algorithm described previously. Some of the conformations were seen to be converging to the same minima after the first stage and these duplicates were removed before the second and final stage of minimisation. Minimisation was terminated when the elements of the first derivatives of energy with respect to the coordinates were less than 10^{-5} kcal mole^{-1} Å^{-1}.

Minimisation of fifty-one tentative conformations resulted in a final count of fourteen unique low-energy conformations of cycloundecane and ten conformations corresponding to energy maxima. All 14 conformations are true local energy minima[26] as evidenced by the calculation of 3N-6 real vibrational frequencies for each, whereas the 10 energy maxima possessed 3N-7 real vibrational frequencies and correspond, therefore, to transition states.

The 14 low-energy conformers of cycloundecane are represented schematically in Figures 2.1 - 2.14 which are arranged in order of increasing V_s. These ORTEP[27] representations are annotated with their ring TAs. It is worth remembering that these calculations produce idealised structures which represent an isolated molecule in the gas phase.

FIG. 2.1 $V_S = 12.67$

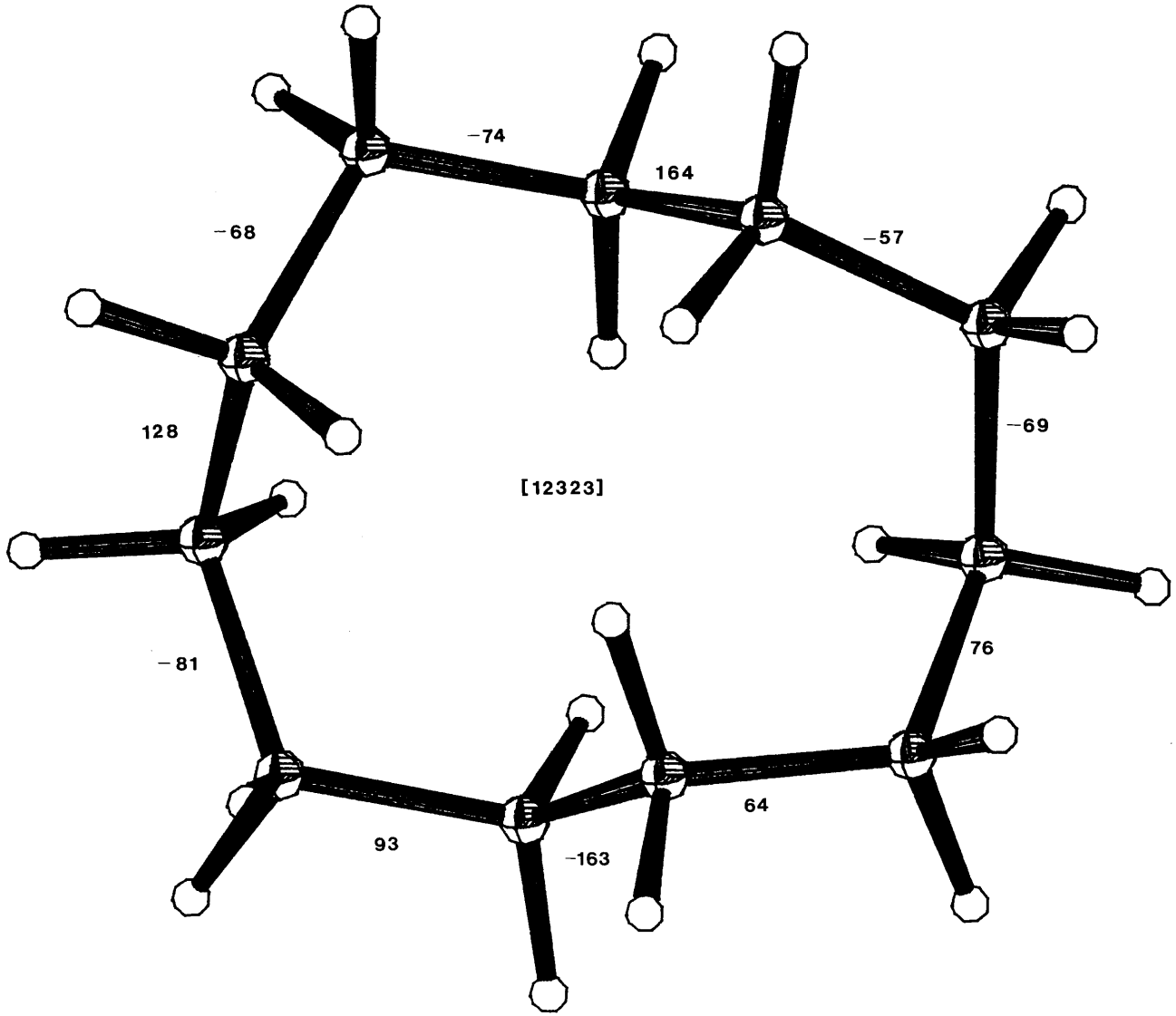


FIG. 2.2 V_s = 13.17

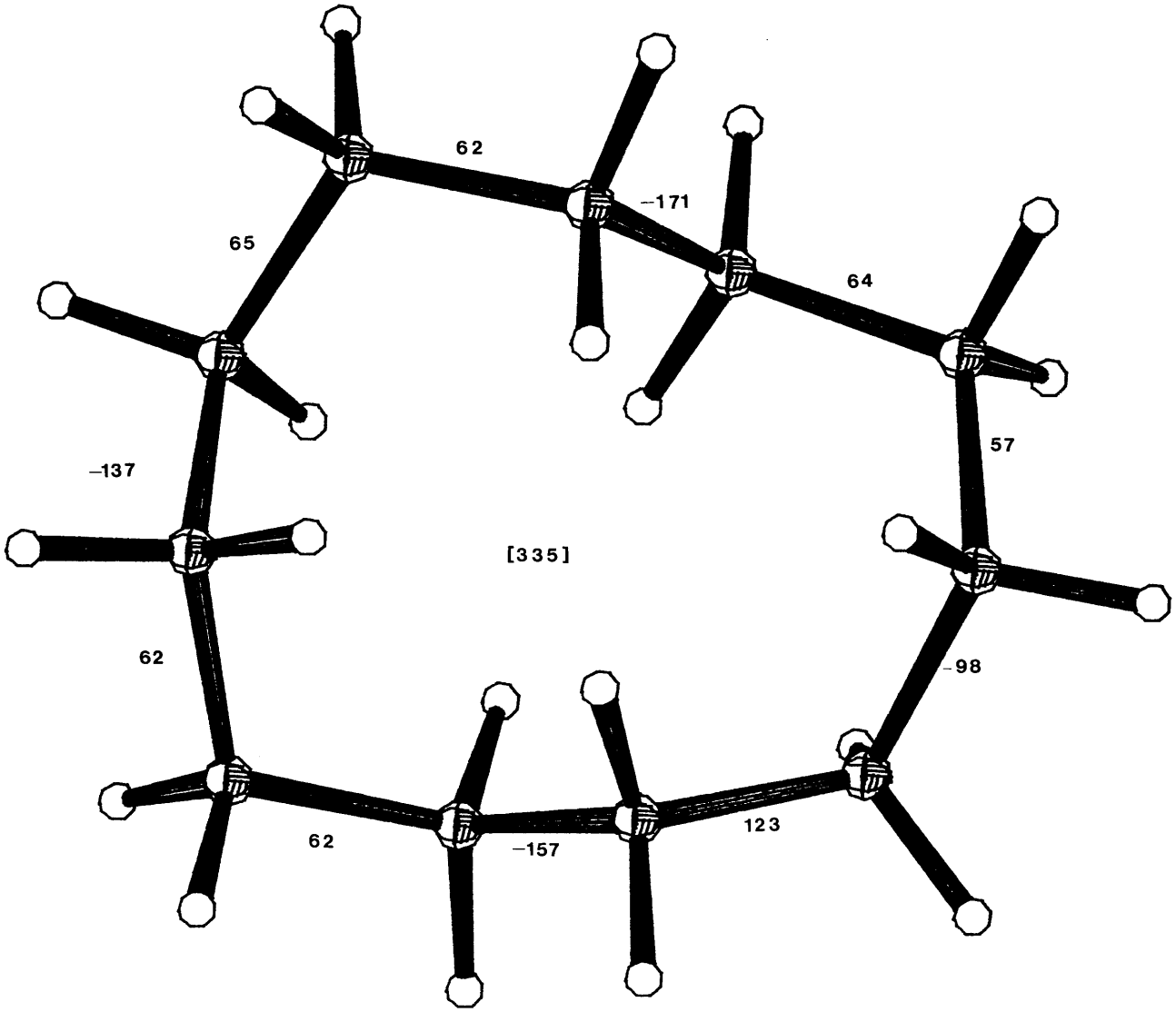


FIG. 2.3 V_s = 13.32

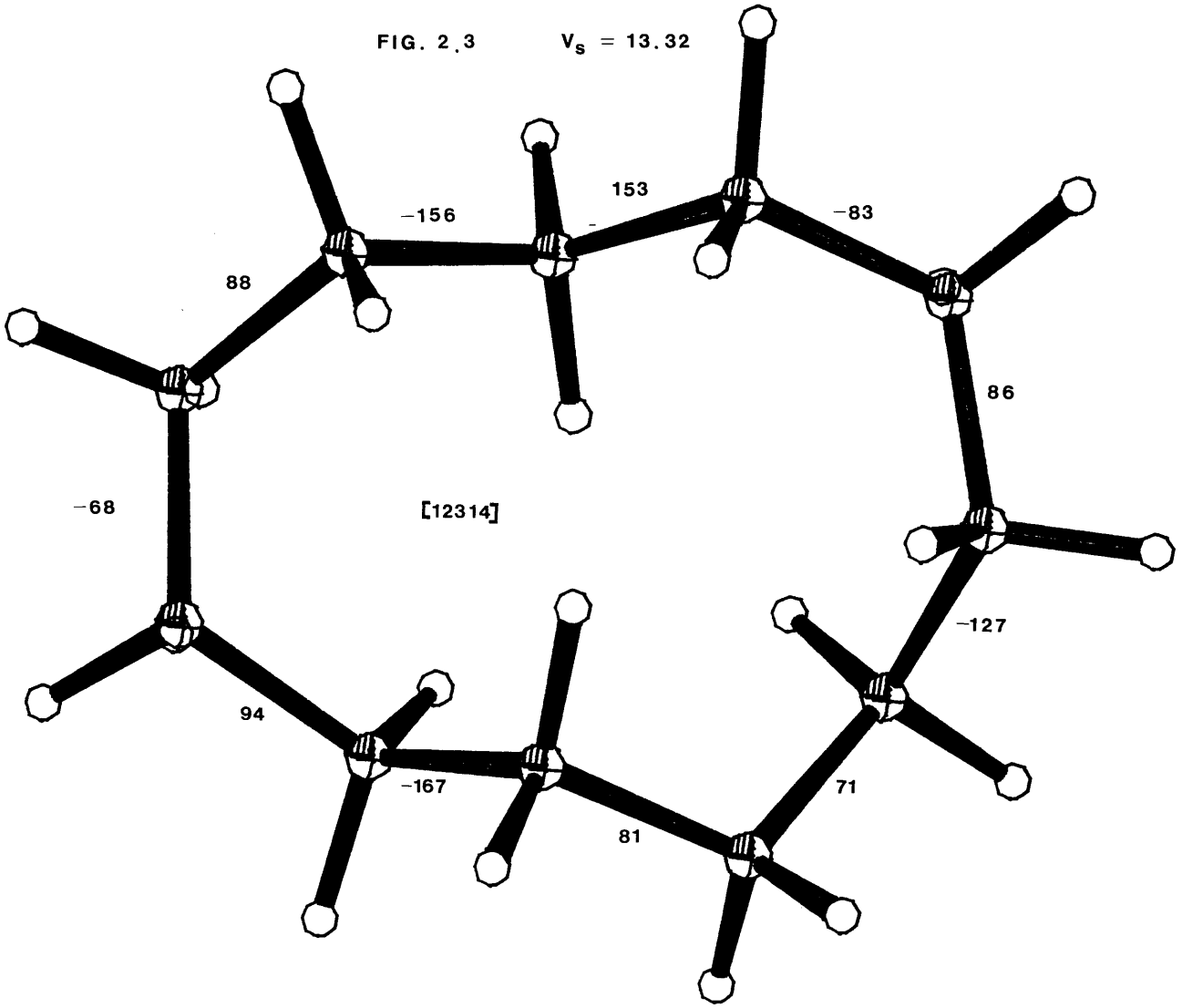


FIG. 2.4 $V_S = 13.50$

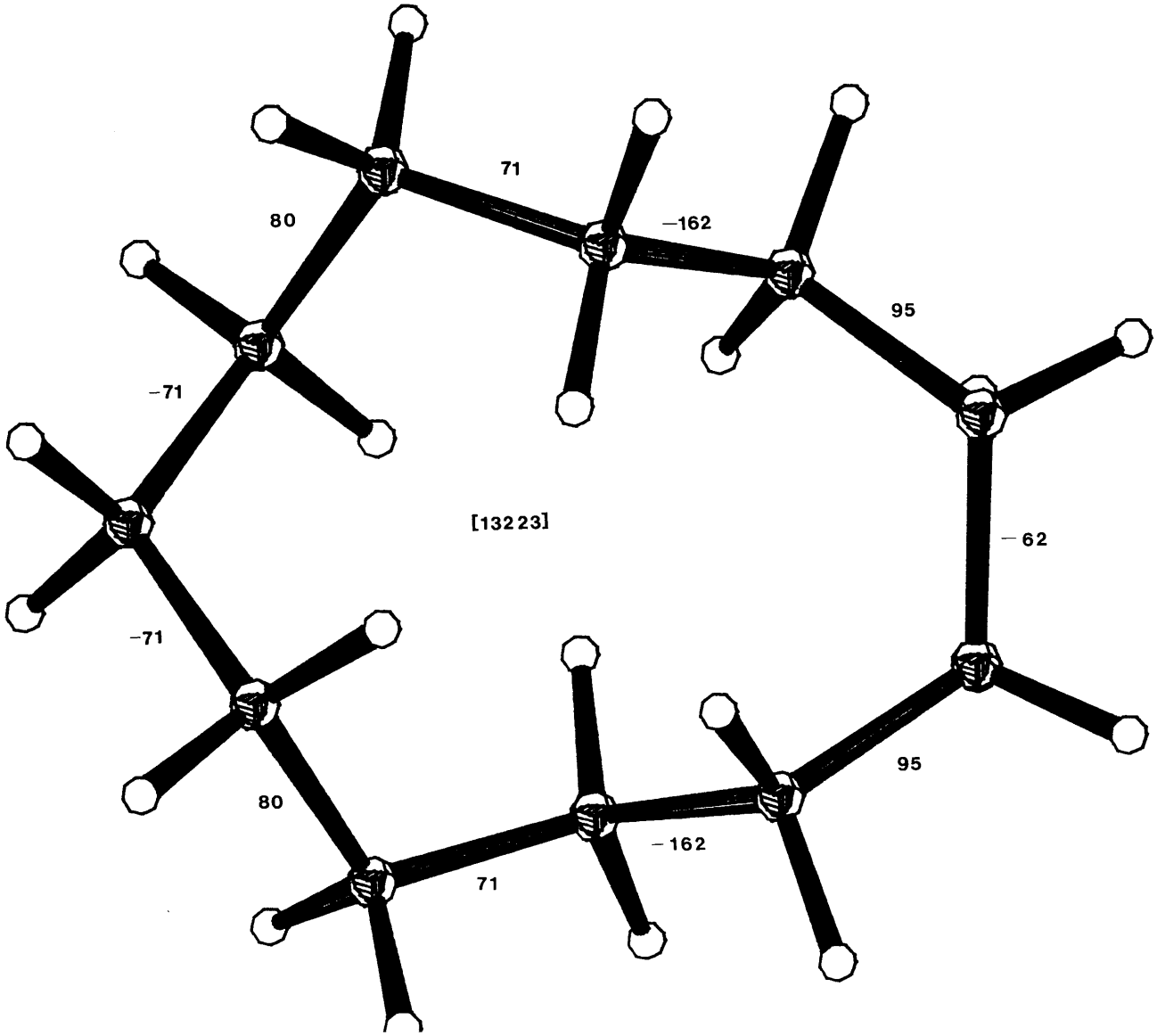
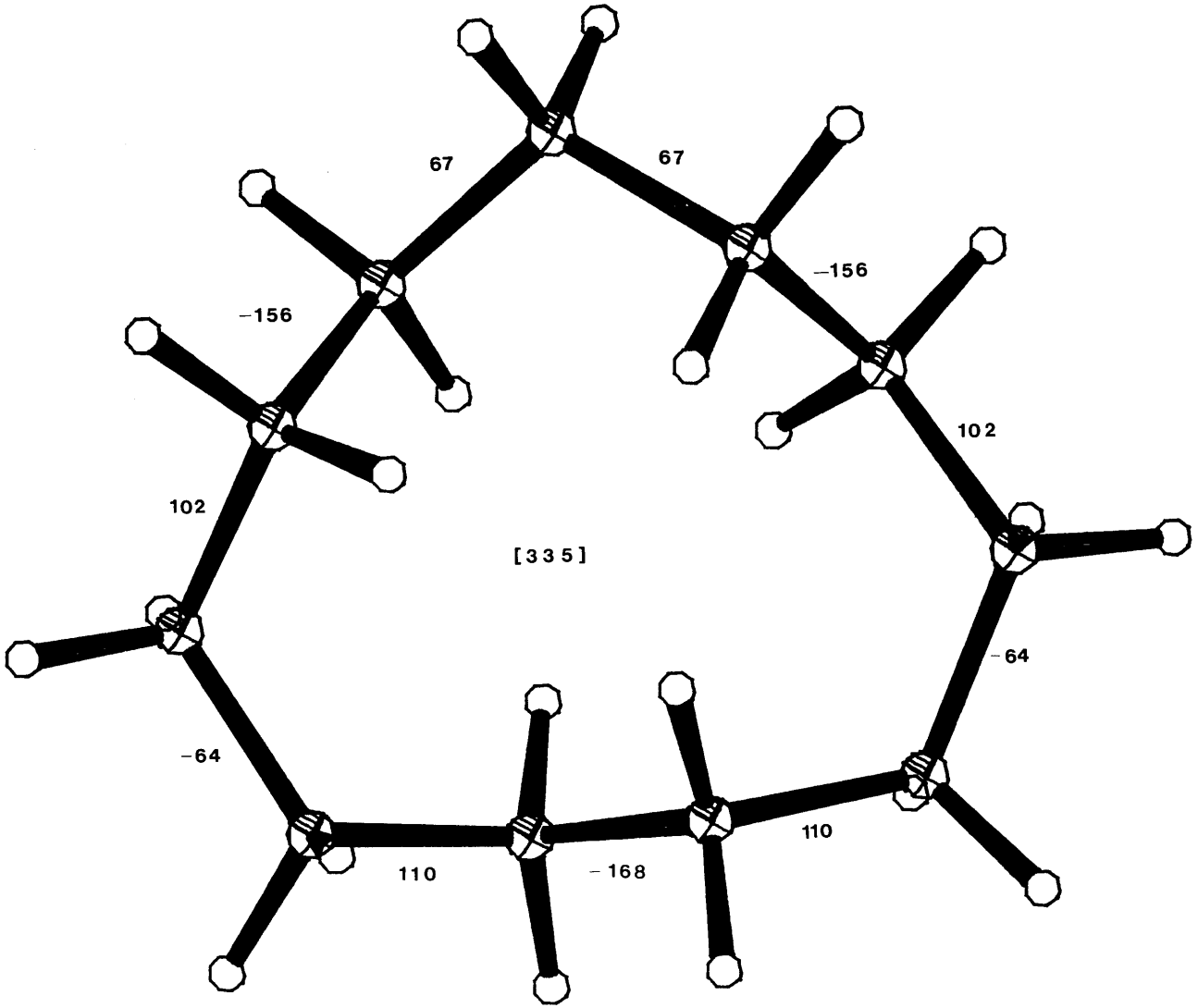


FIG. 2.5 $V_S = 14.19$



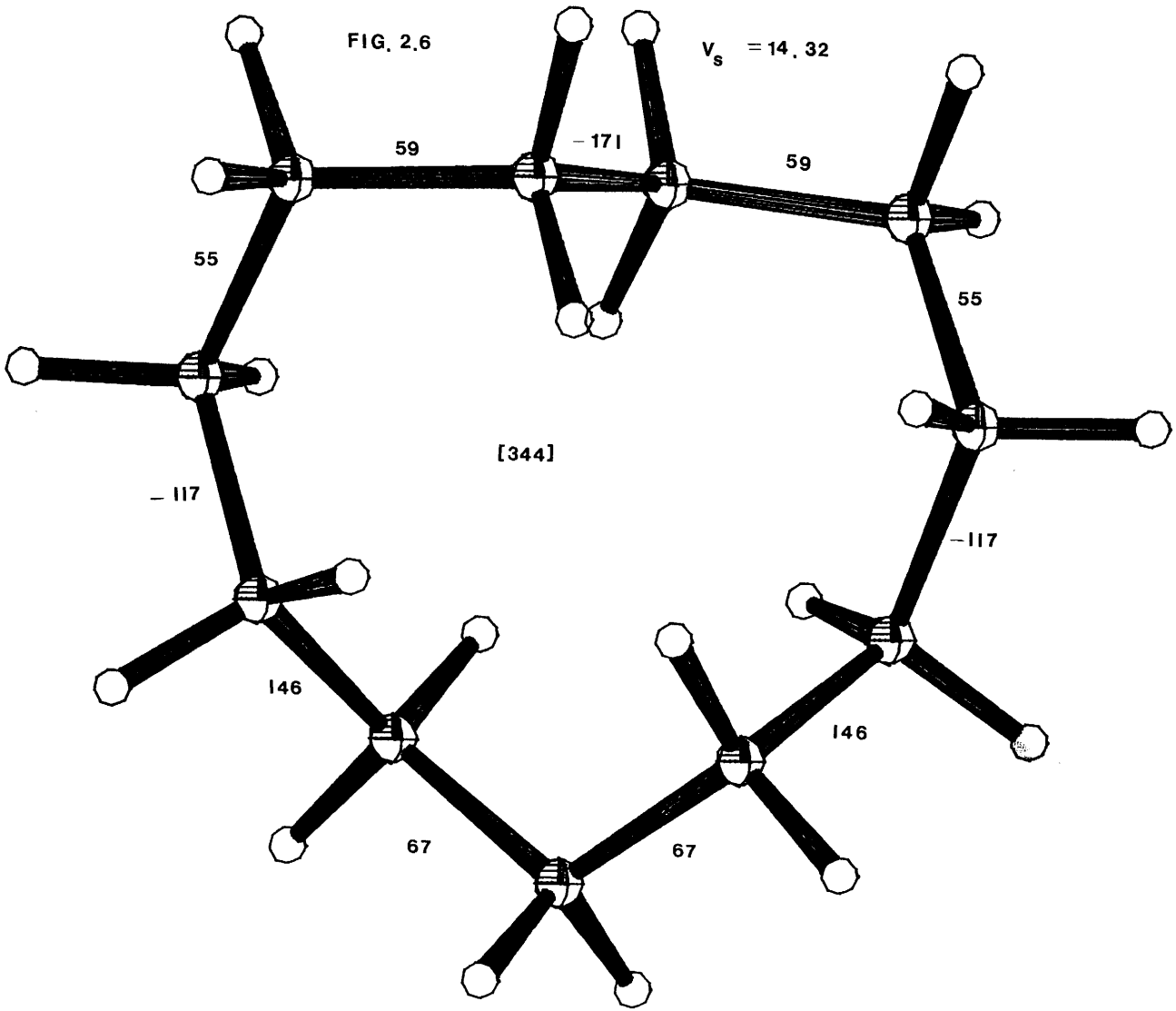
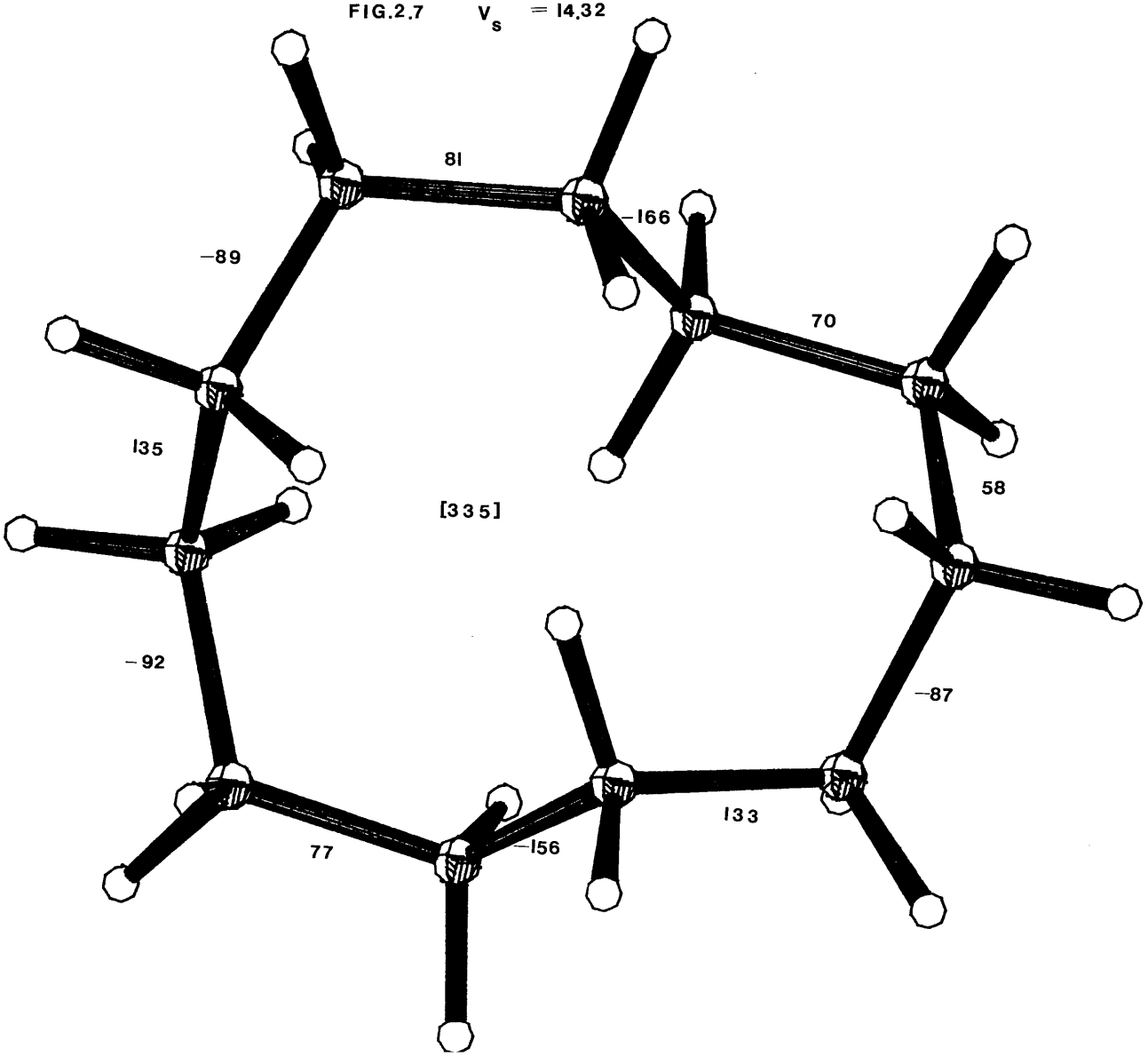


FIG. 2.6
V_s = 14.32
59
-171
59
55
55
[344]
-117
-117
146
146
67
67

FIG.2.7 V_s = 14.32



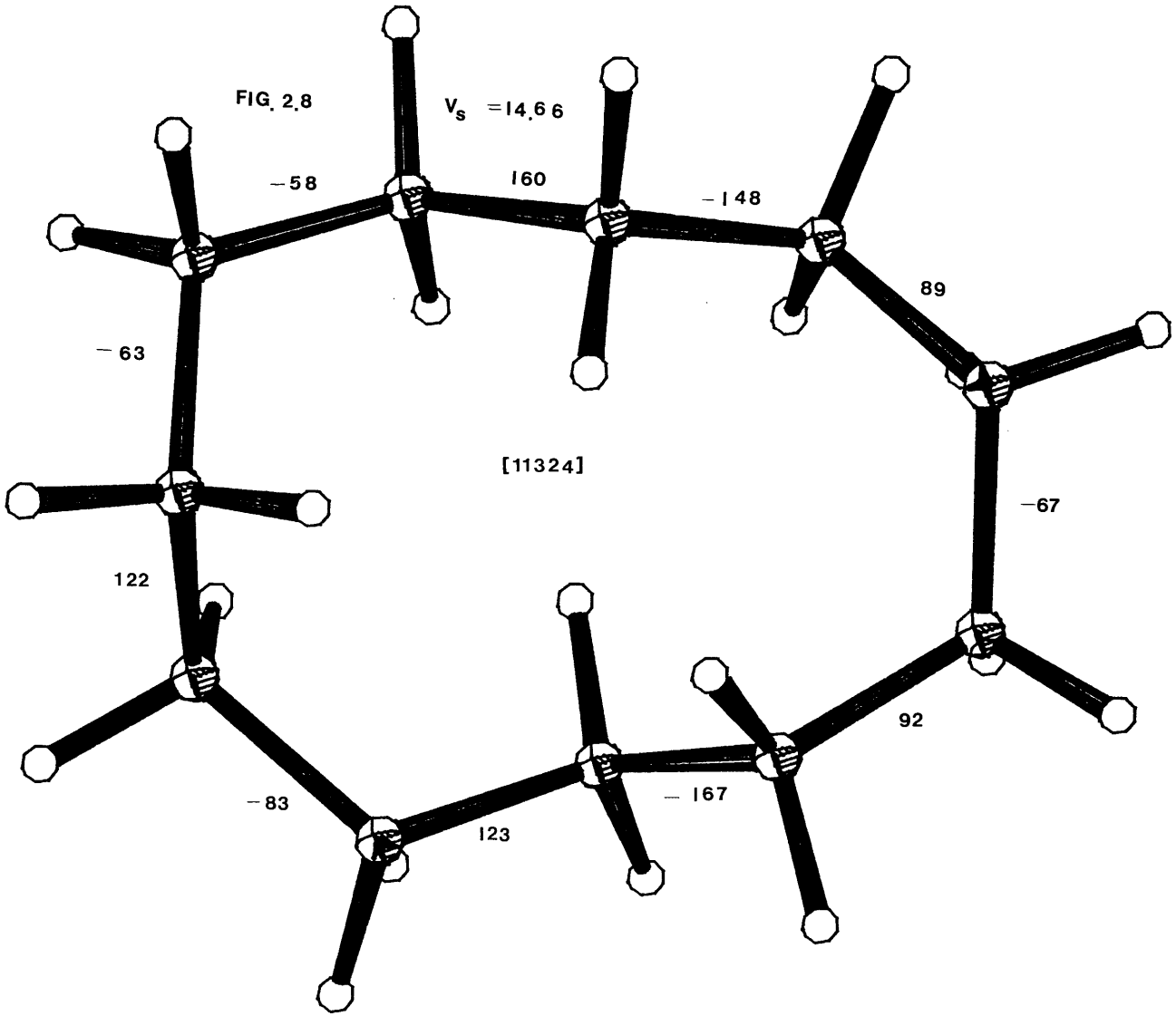
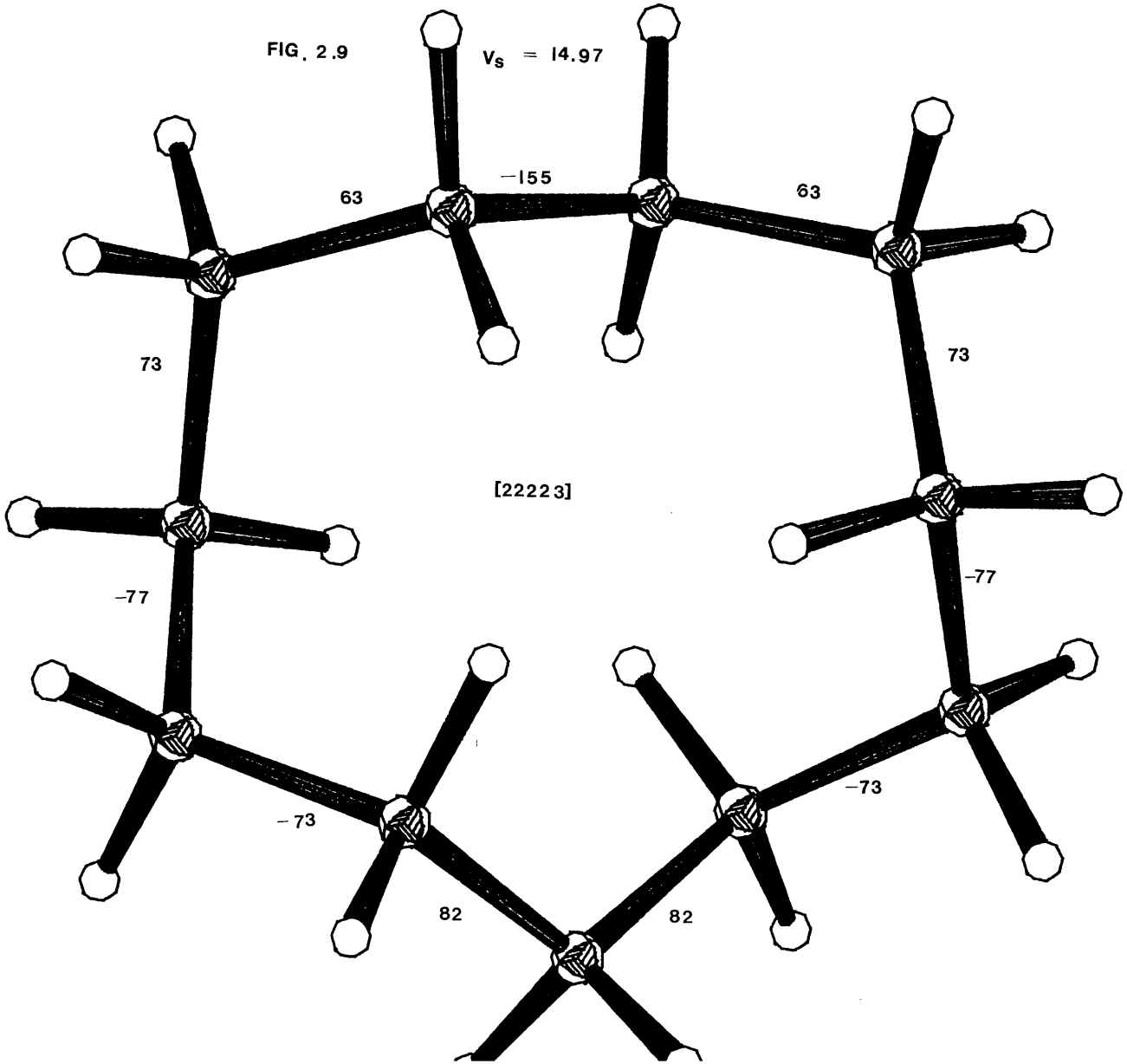


FIG. 2.8
V_s =14.66
−58
160
−148
89
−63
[11324]
−67
122
92
−83
123
−167

FIG. 2.9



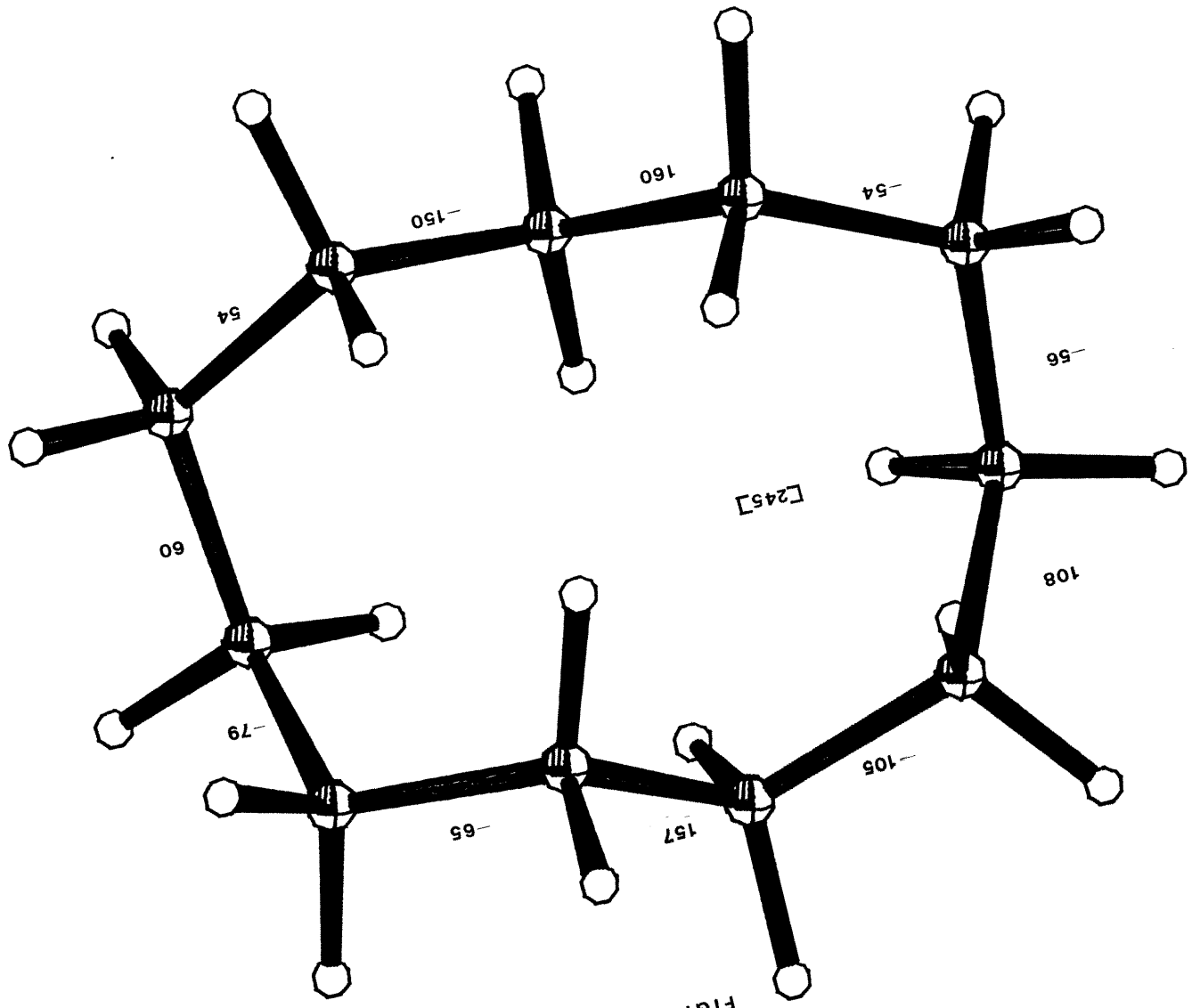
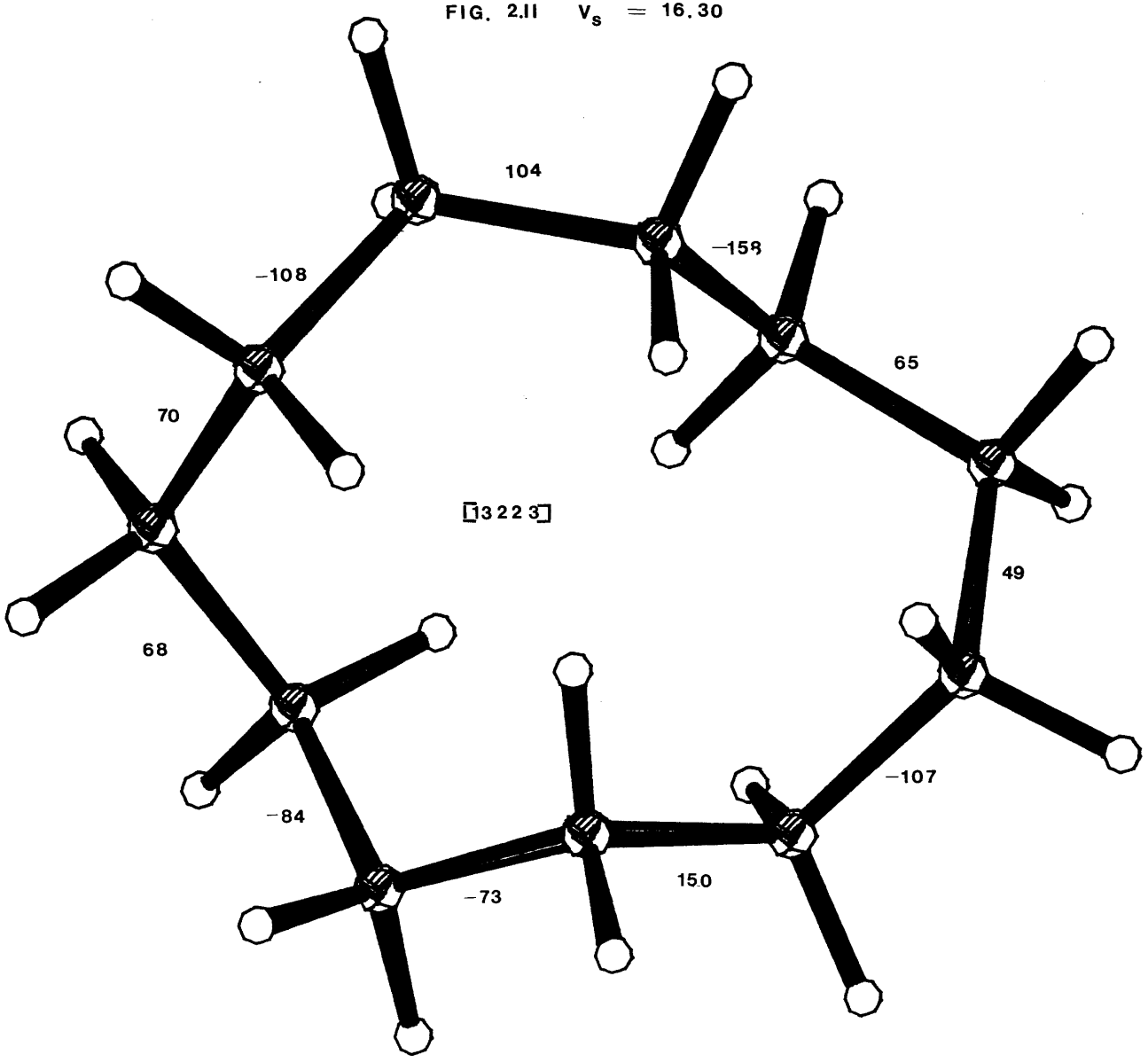


FIG. 2.10 $V_s = 15.27$

FIG. 2.11 $V_s = 16.30$



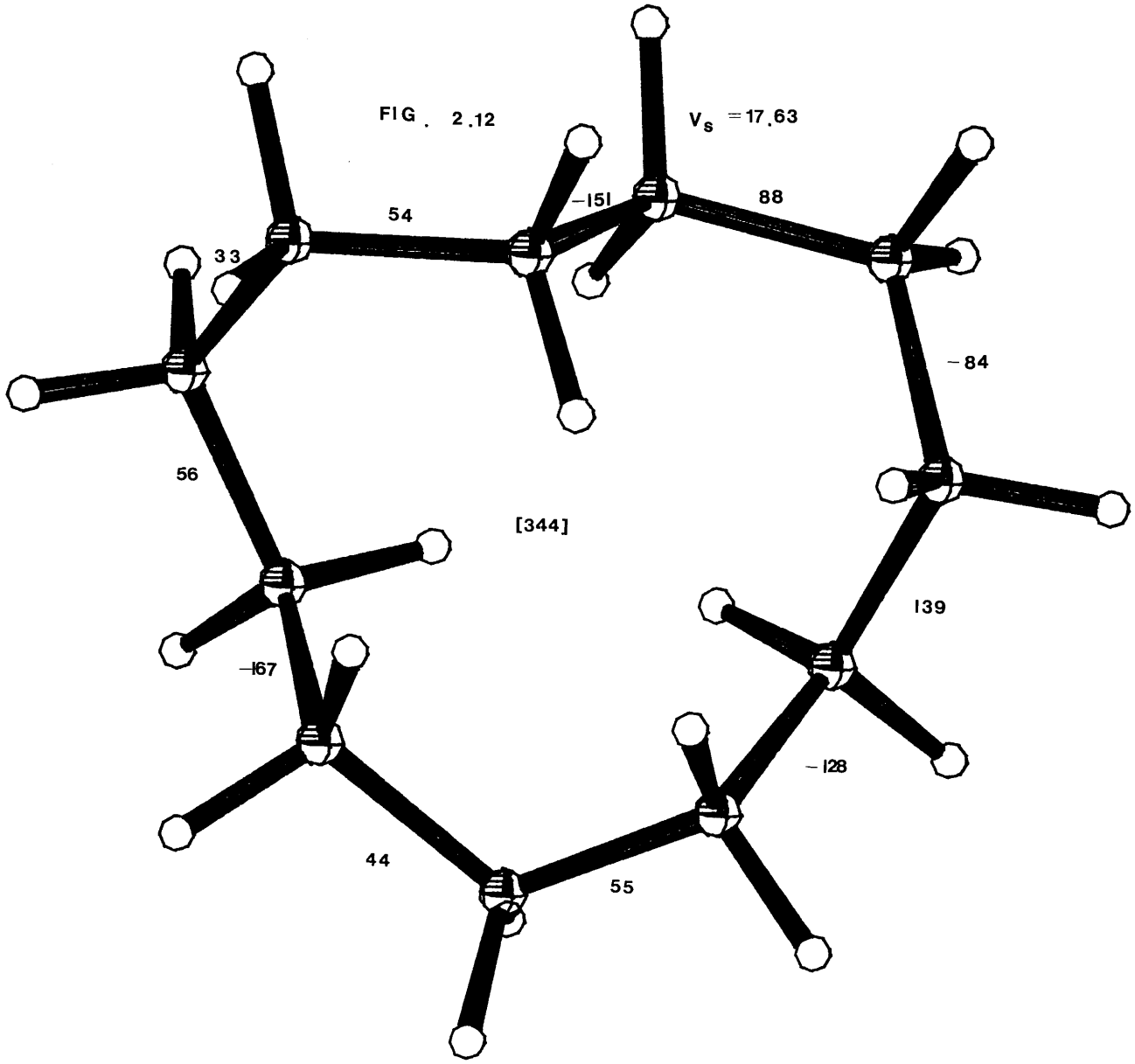


FIG. 2.12
V_s = 17.63
54
-151
88
33
-84
56
[344]
139
-167
-128
44
55

FIG. 2.13 $V_S = 19.87$

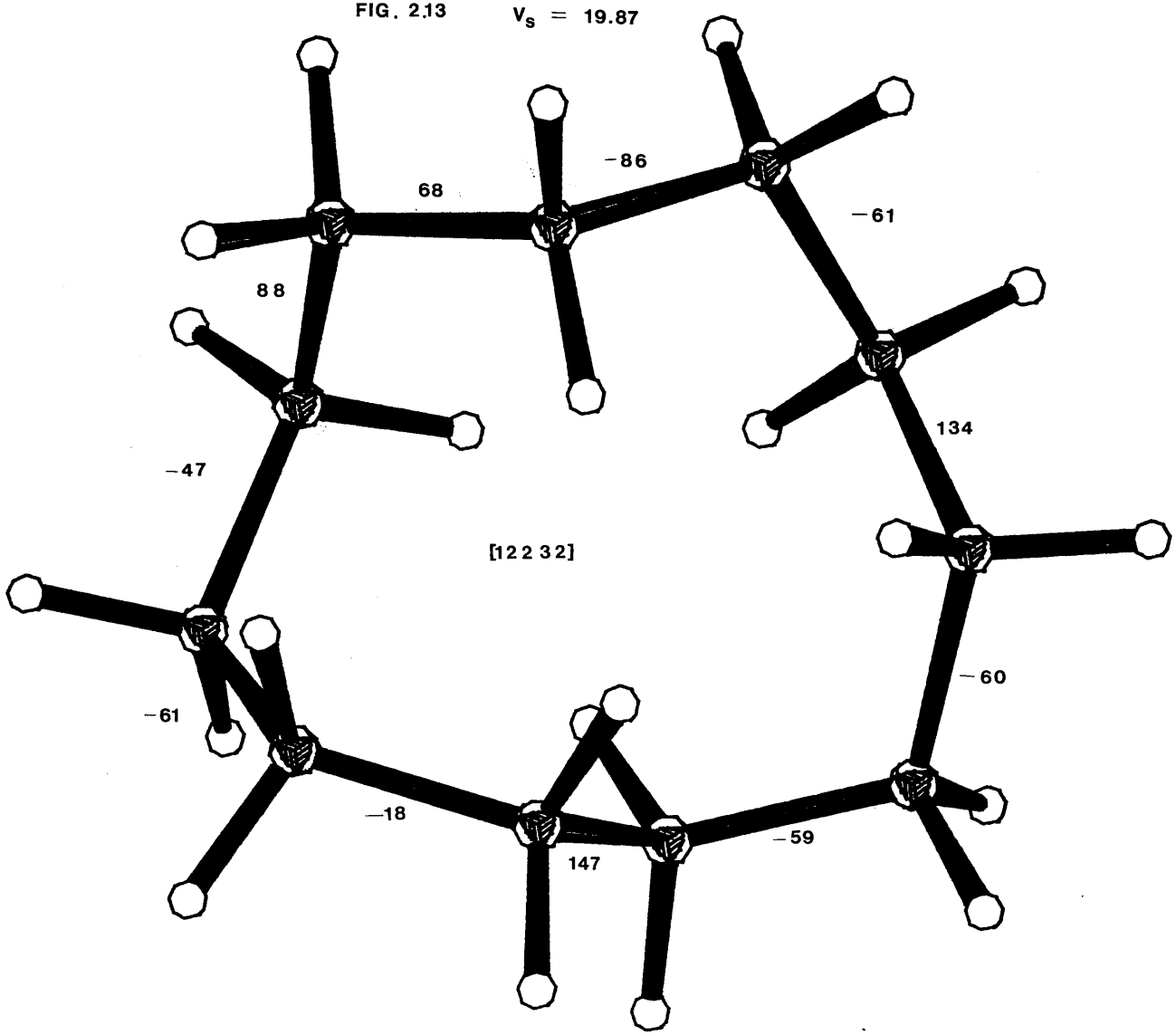


FIG. 2.14 $V_S = 23.16$

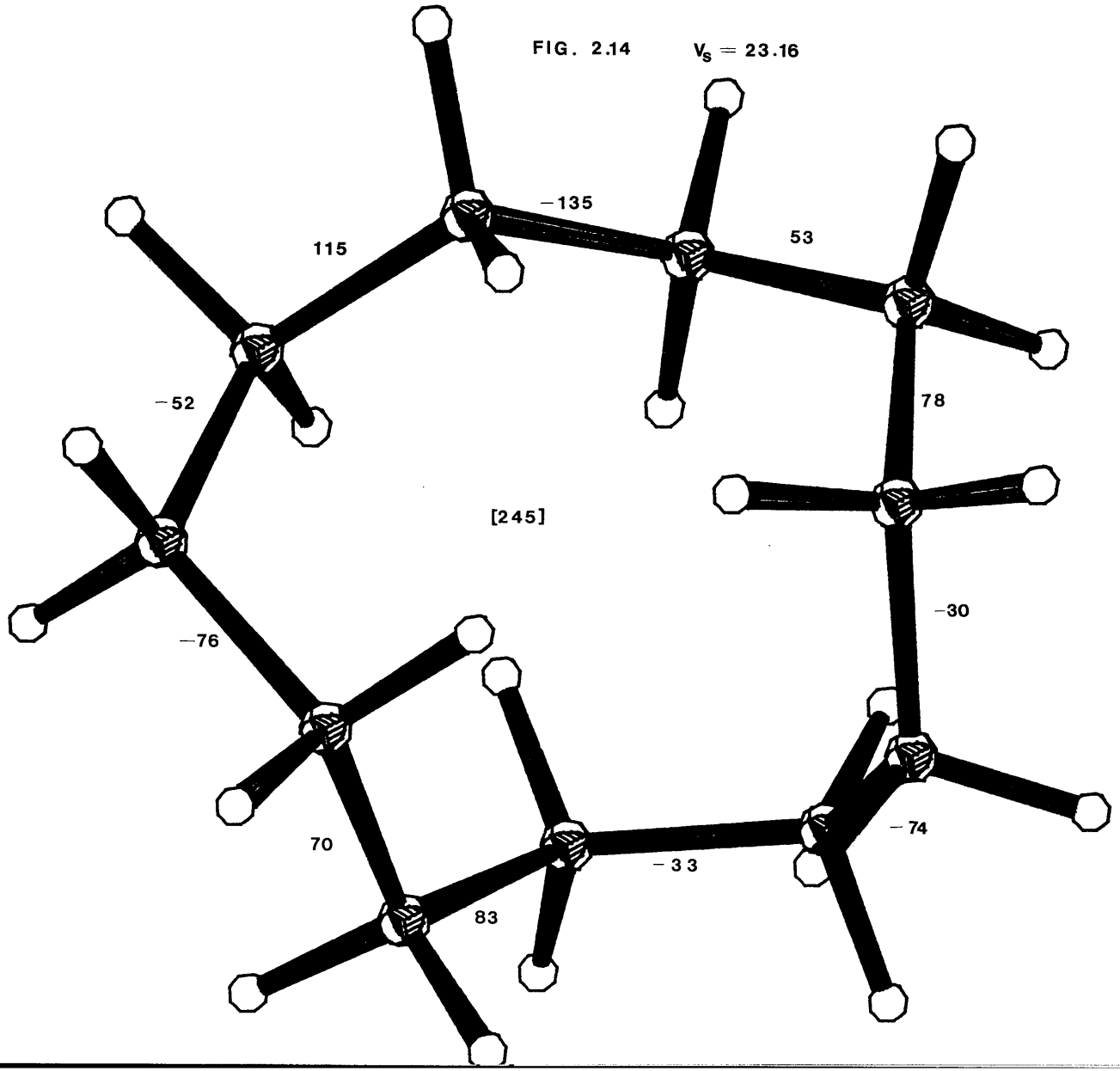


FIG. 2.15 $V_s = 14.17$

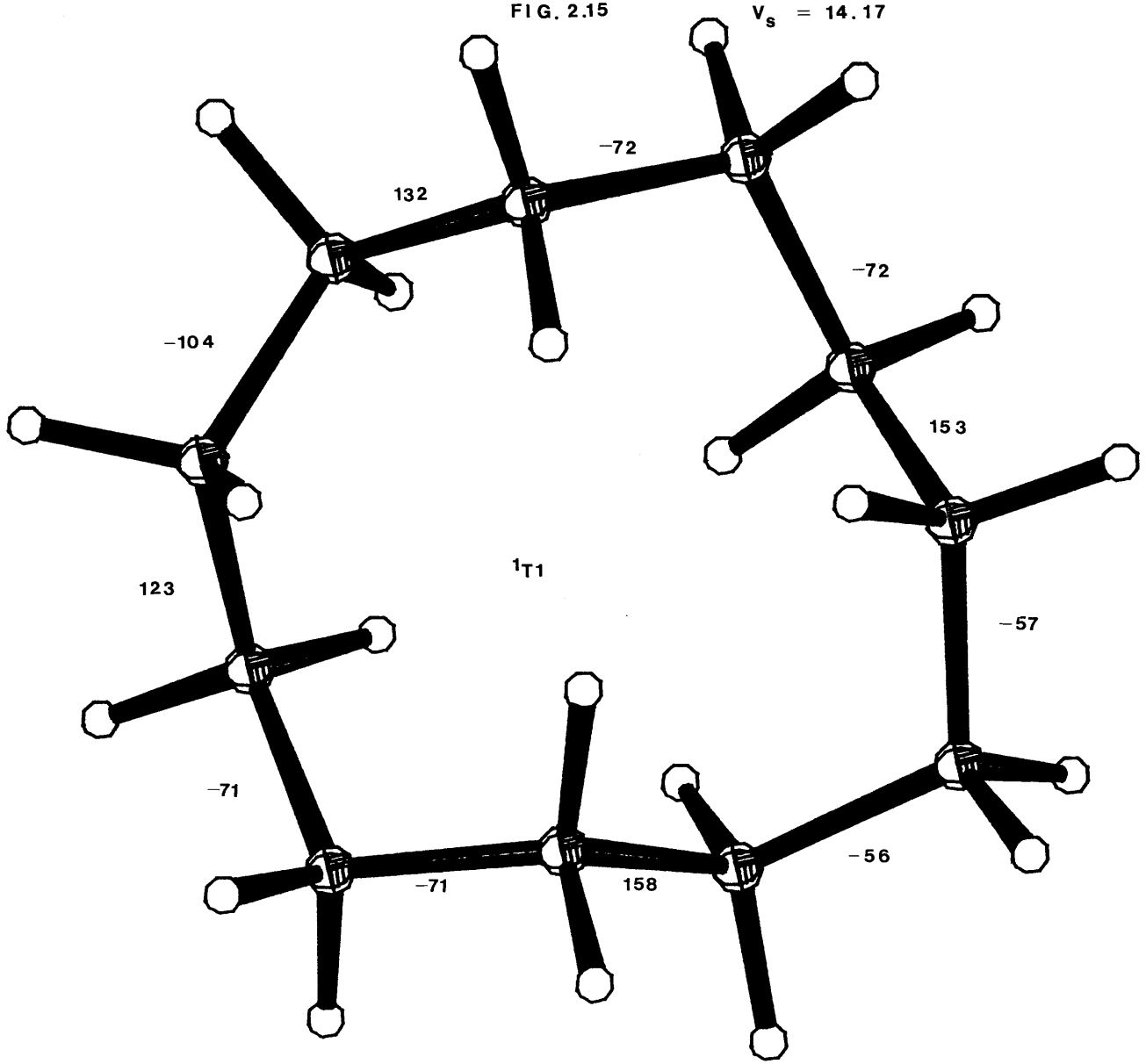


FIG. 2.16 $V_s = 14.17$

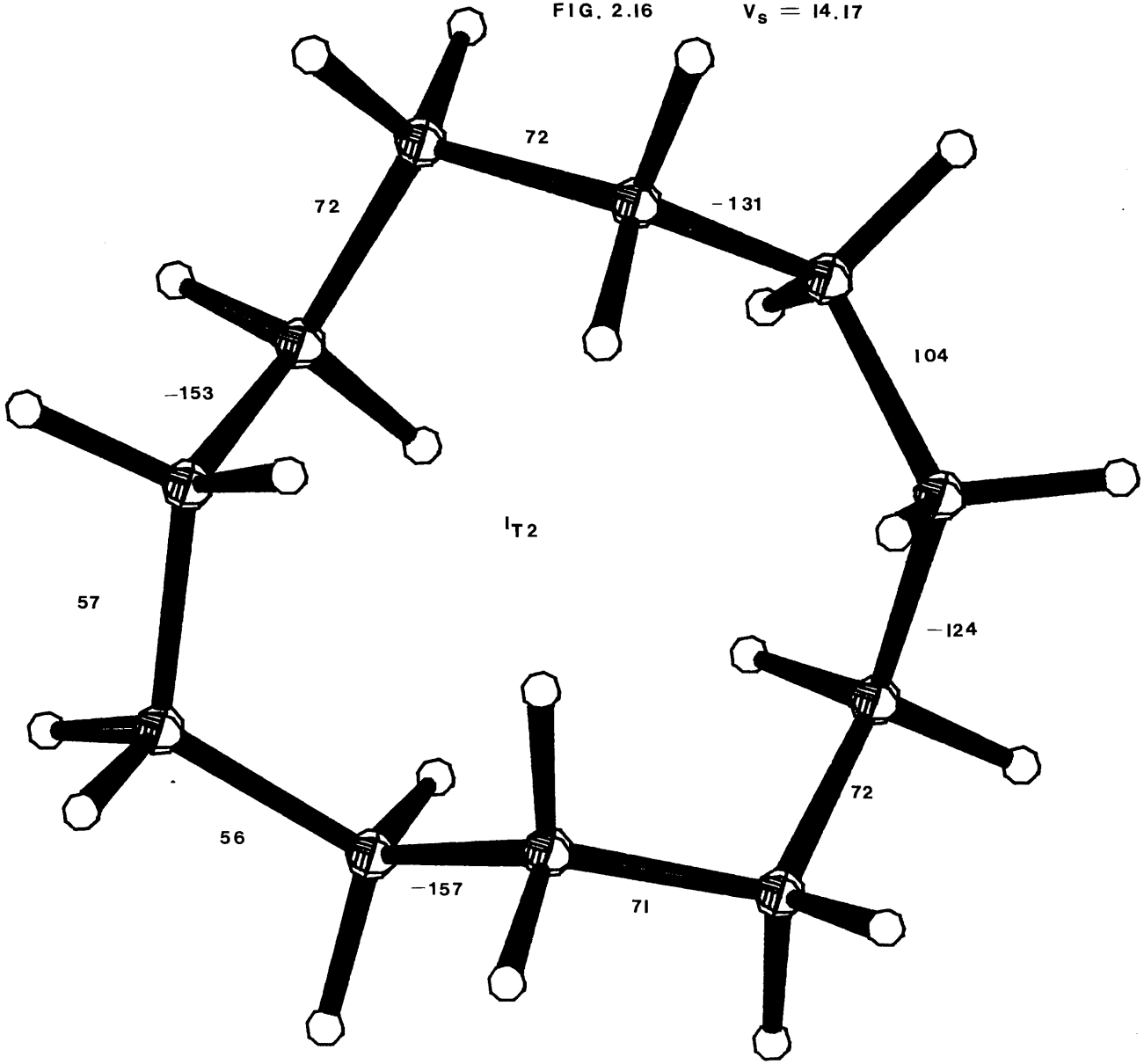


FIG. 2.17

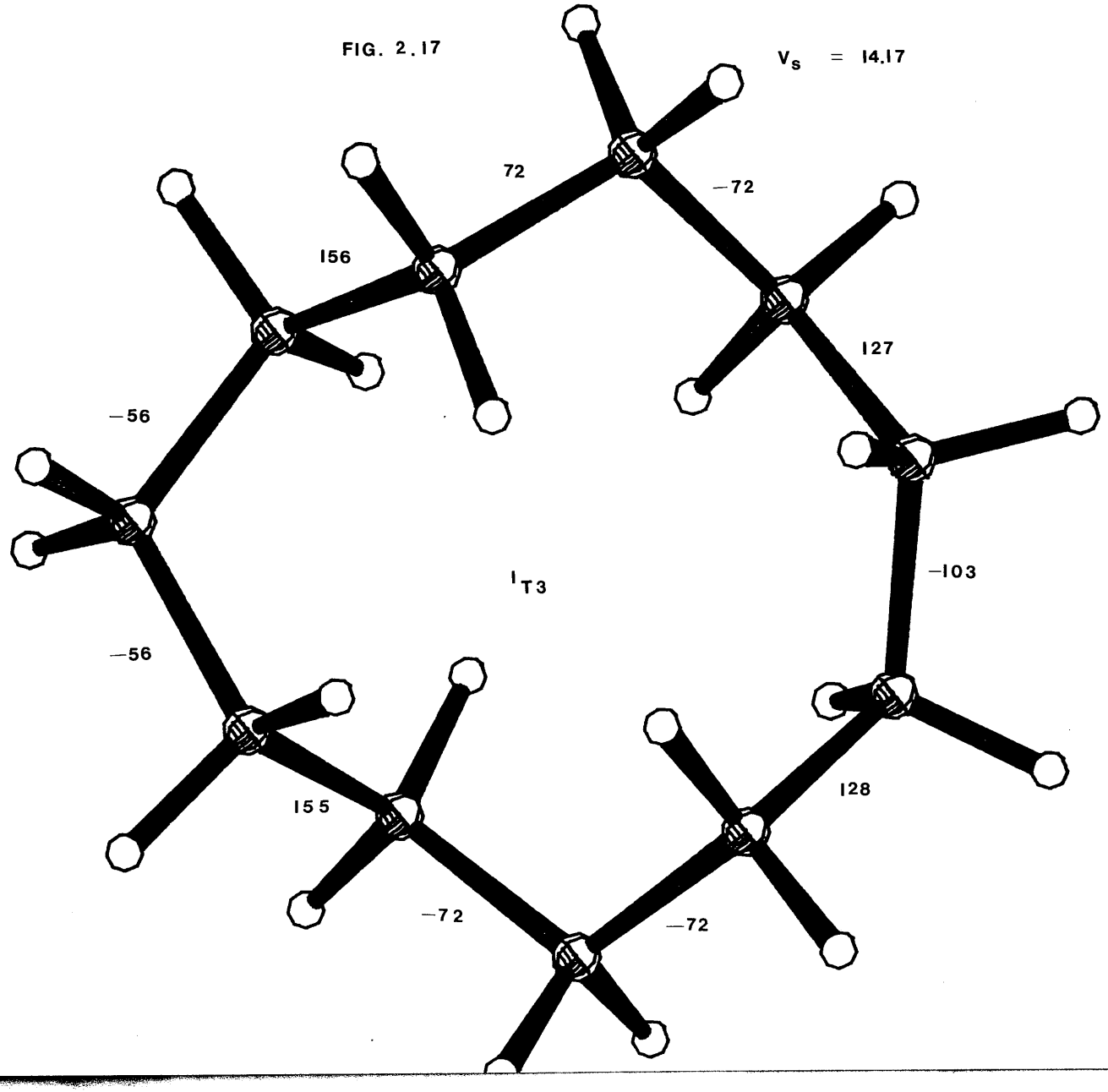


FIG. 2.18 $V_S = 14.23$

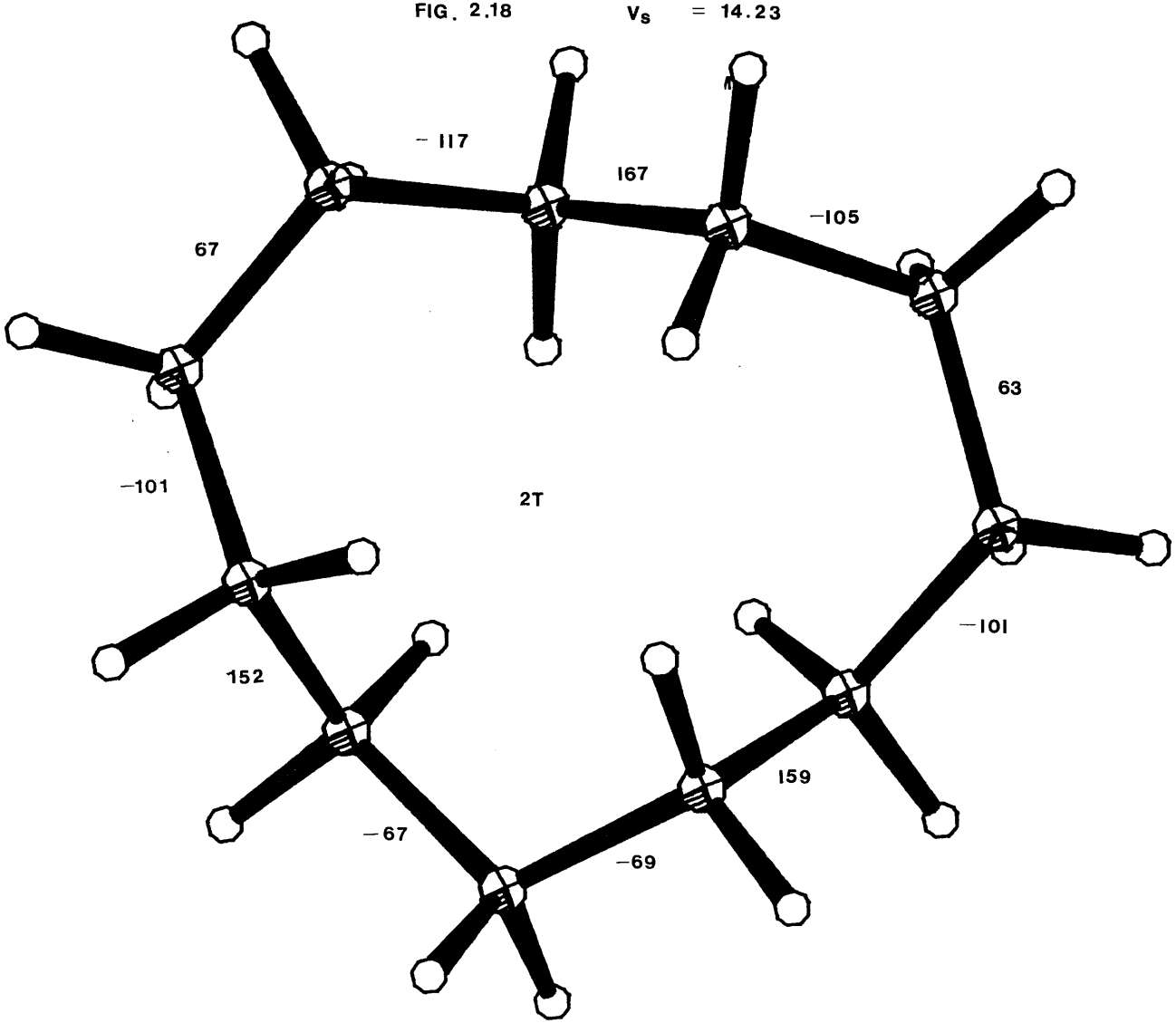


FIG. 2.19 $V_s = 15.09$

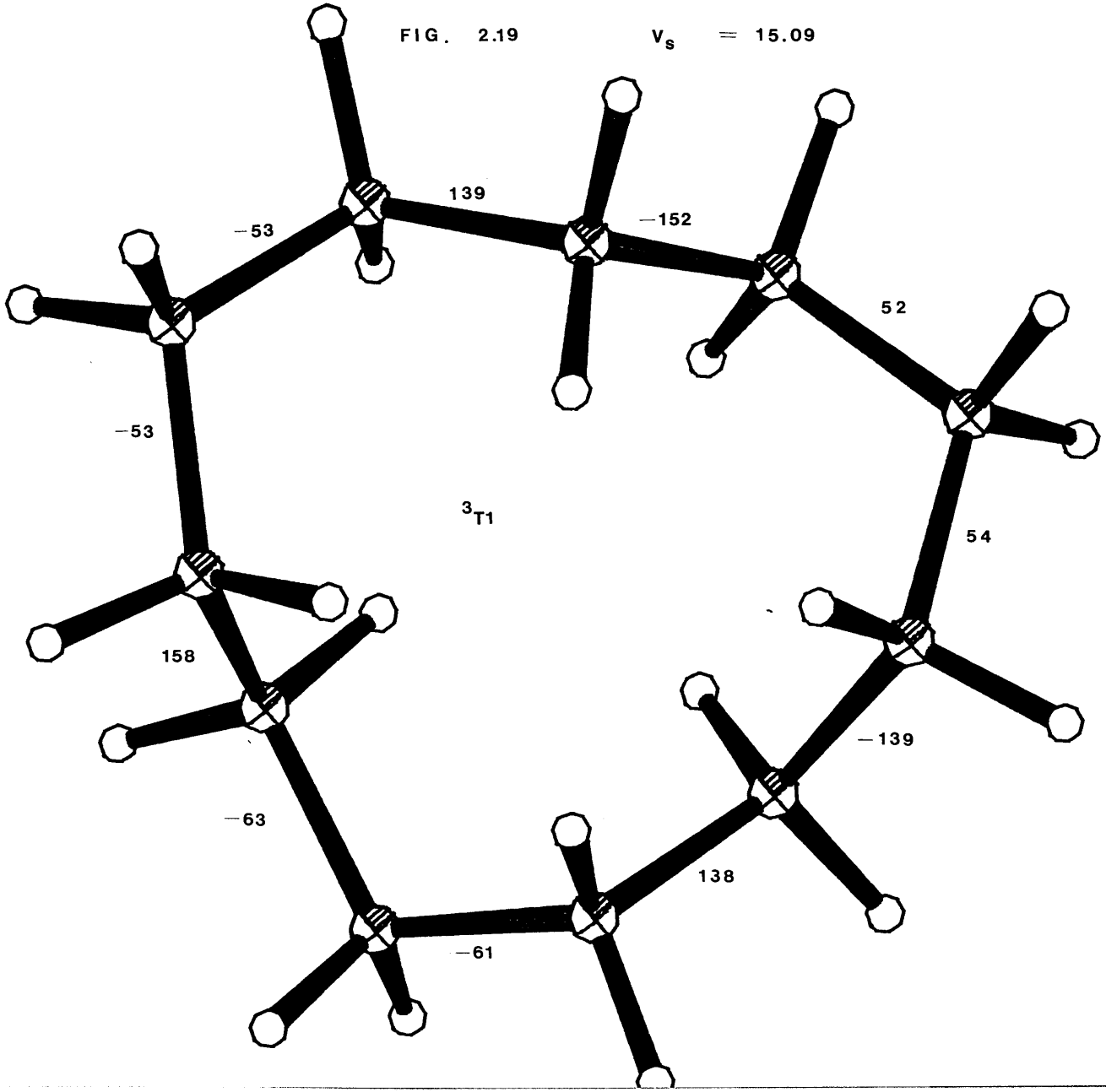


FIG. 2.20 $V_s = 15.09$

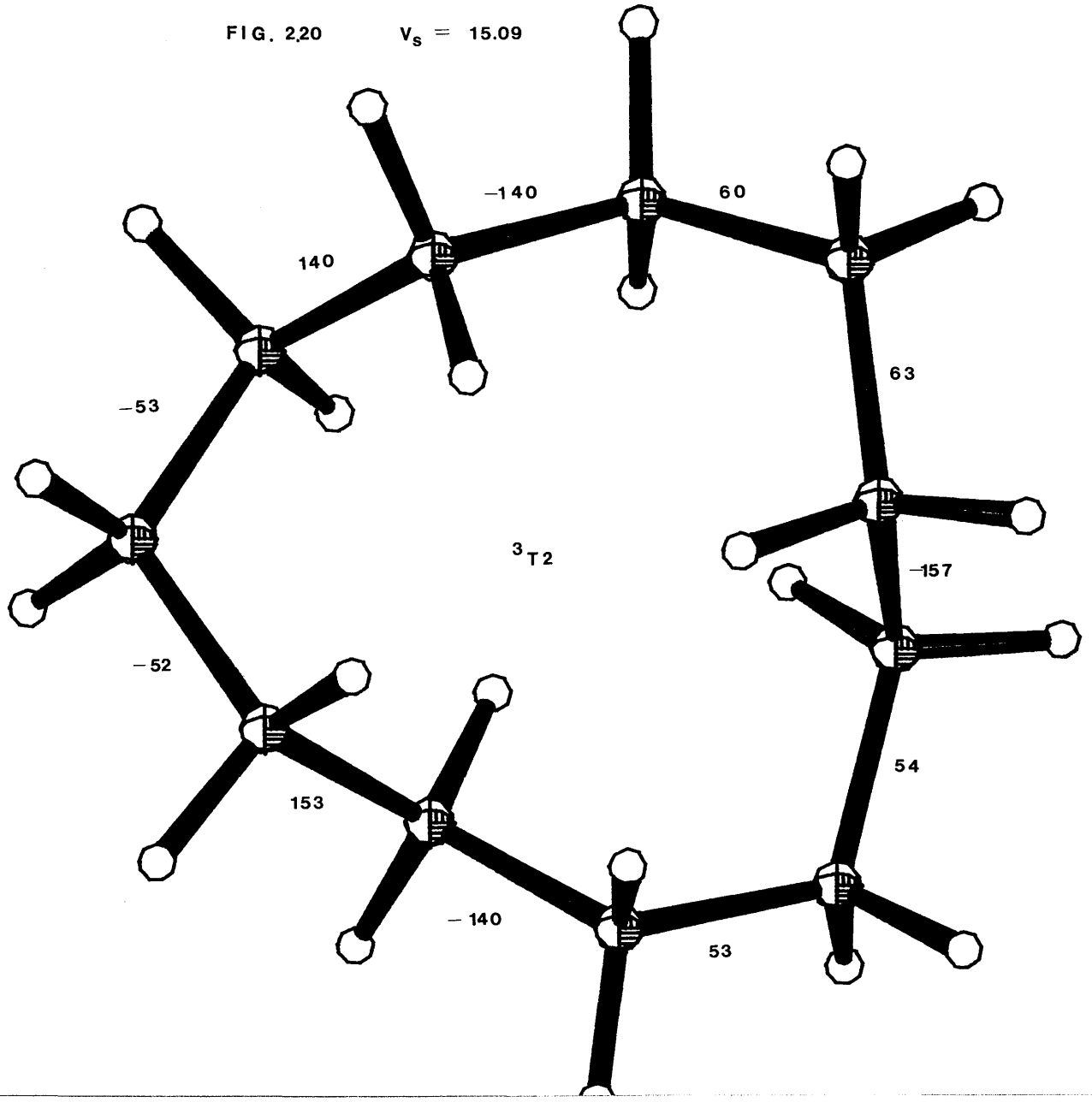
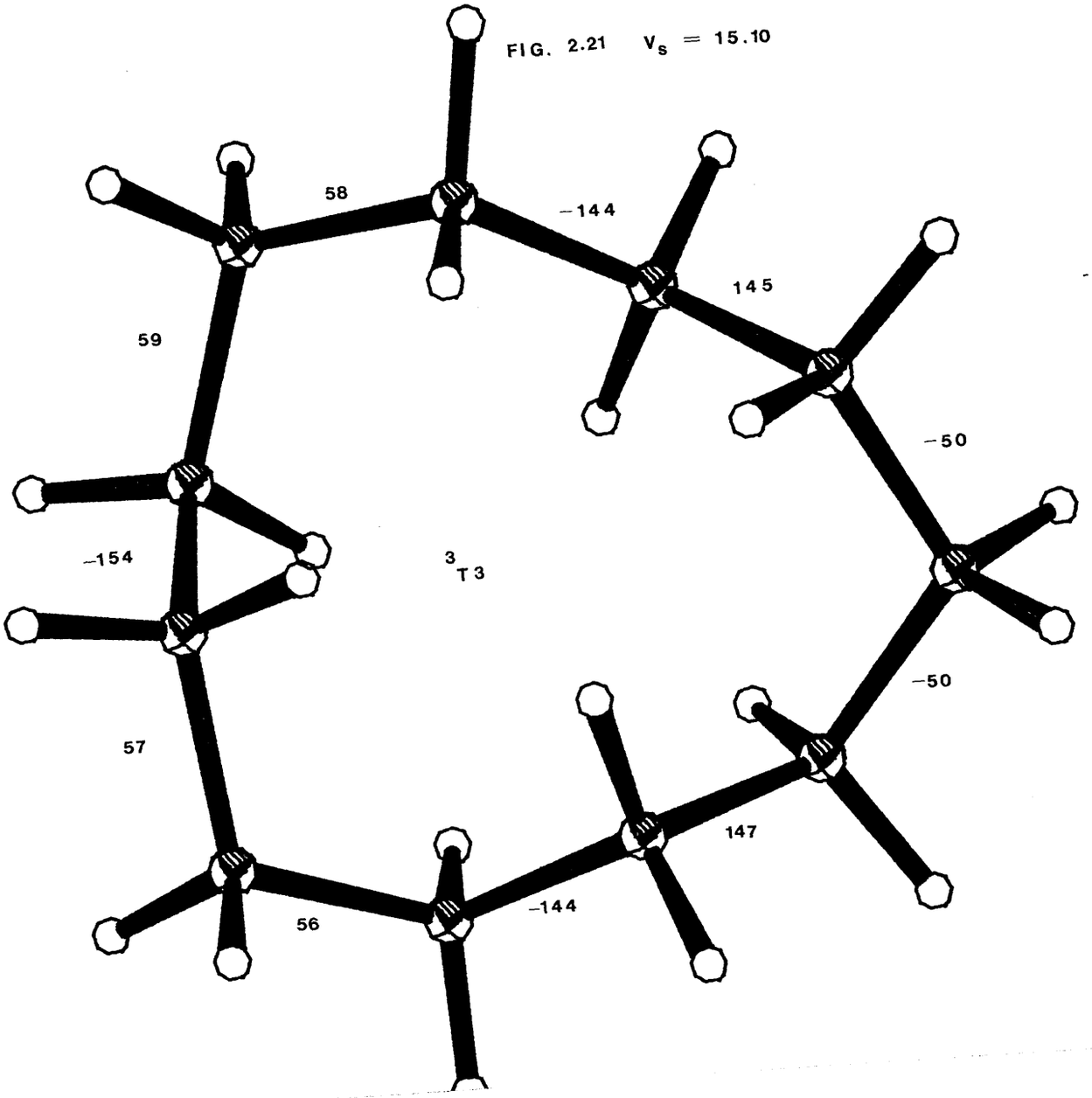


FIG. 2.21 $V_s = 15.10$



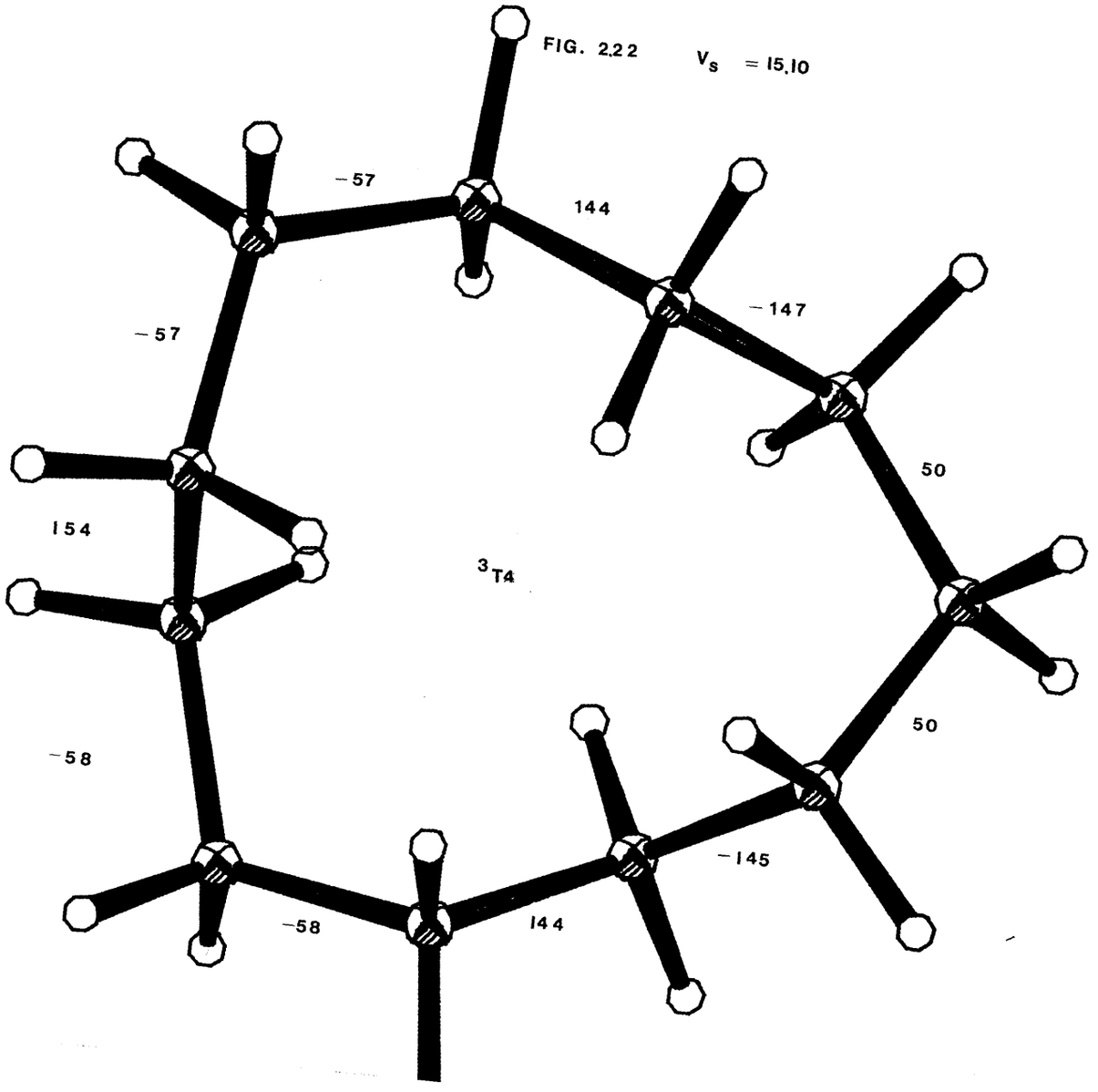


FIG. 2.22
V_S = 15.10
−57
144
−147
−57
50
154
$^3T_4$
50
−58
−145
−58
144

FIG. 2.23 V_s = 15.38

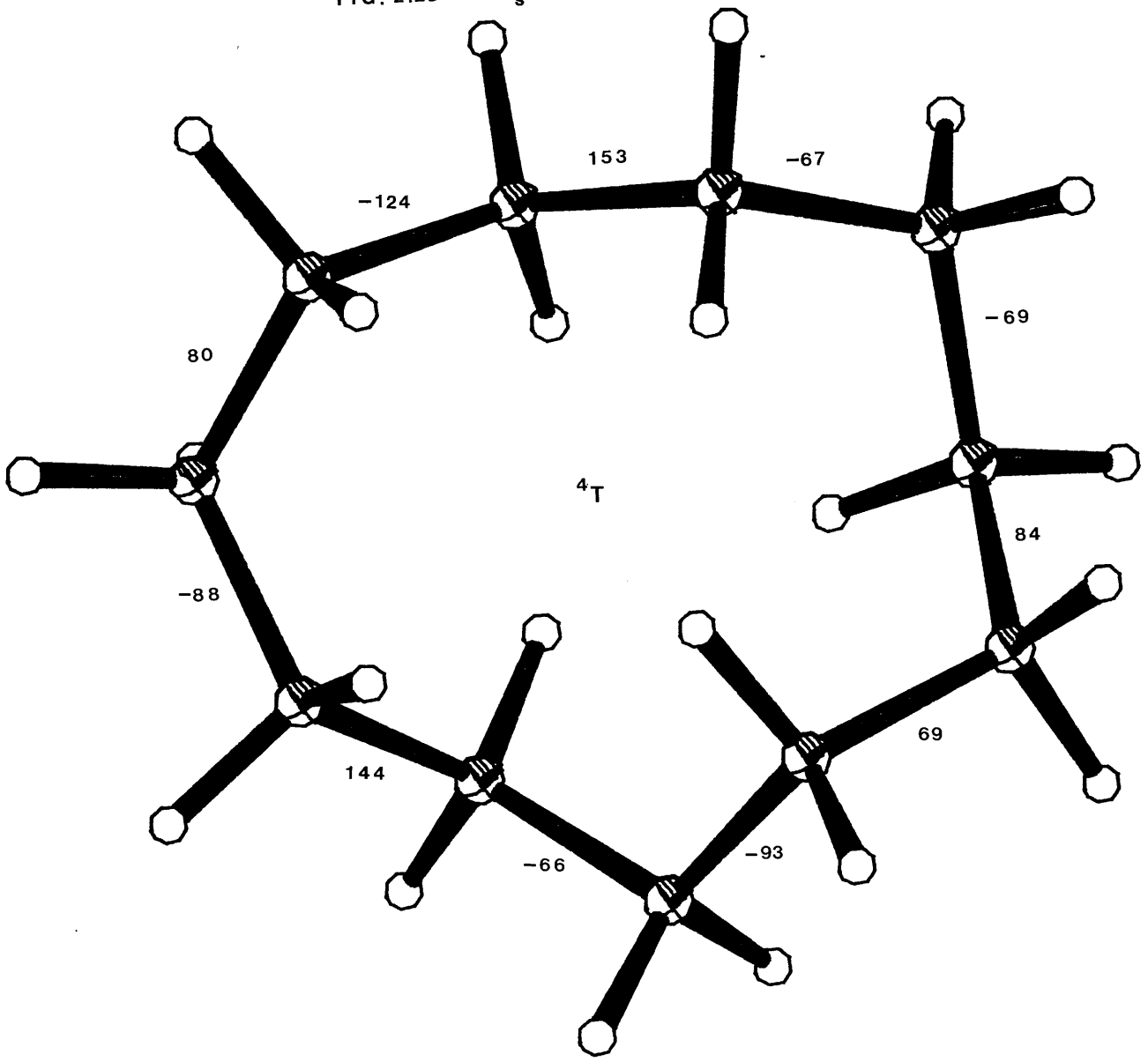
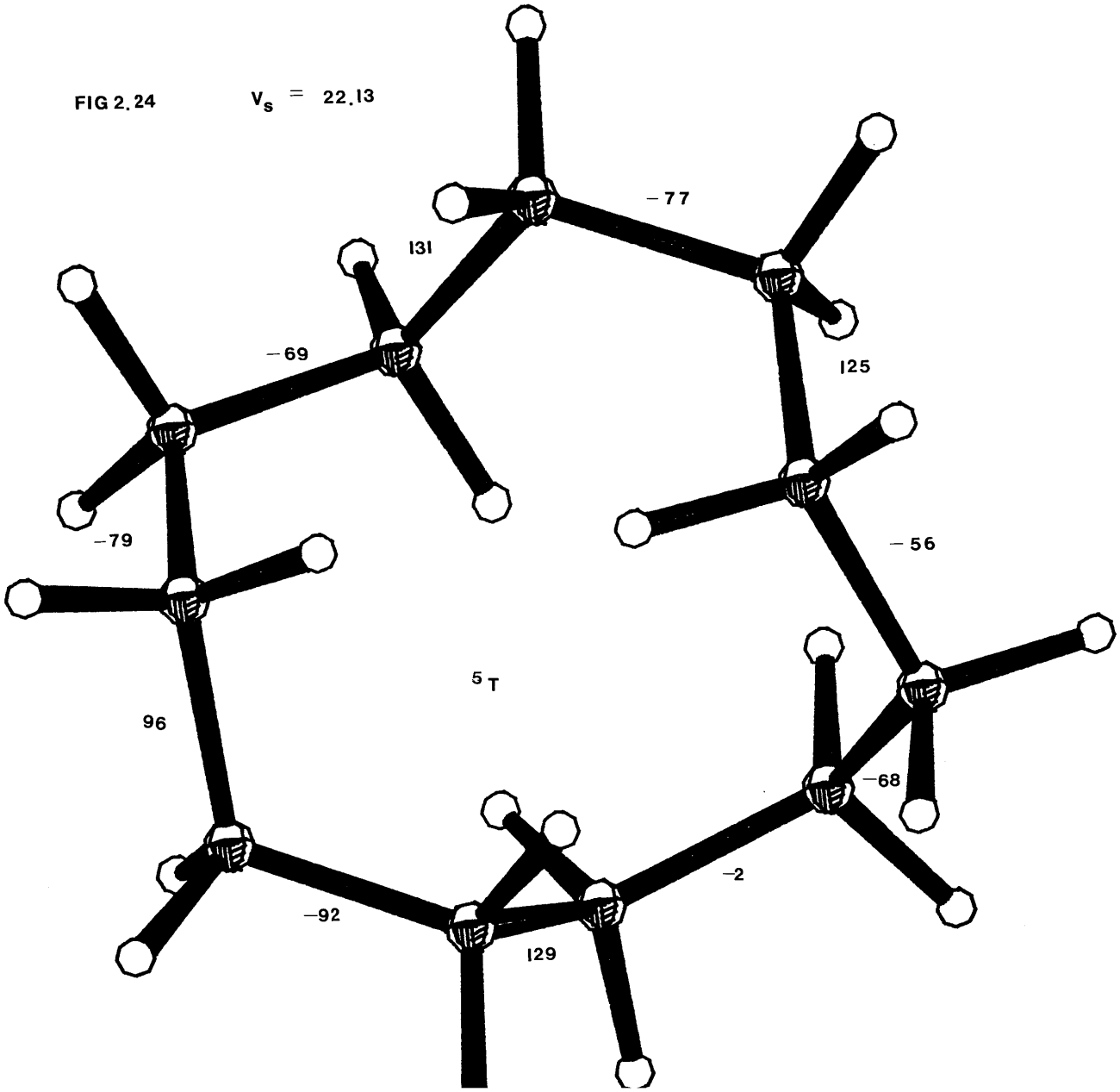


FIG 2.24 $V_s = 22.13$



The 10 transitional conformations are drawn in Figures 2.15 - 2.24 which are also arranged in order of increasing V_s and annotated with ring TAs.(°)

MM calculations predict the existence of 10 low-energy conformers for cycloundecane differing in V_s by 3 kcal $mole^{-1}$ or less, with a quinquangular GMEC, [12323], only 0.49 kcal $mole^{-1}$ energetically more stable than the next conformation - a triangular [335]. Table 1 records the V_s of each of the 14 low energy conformations of cycloundecane.

The energy minimisation procedure minimises the energy with respect to the cartesian coordinates and supplies the detailed geometry, the steric energy components and the total V_s, of different conformational minima of one molecule. The V_s corresponds to an isolated molecule in a "hypothetical motionless state at $0^{\circ}K$ "[28]. In order to compare the calculated V_s of a molecule with an experimental quantity, usually the heat of formation, ΔH_f^0, (which is defined as the heat absorbed or released upon formation of the compound from the standard states of the elements composing it) it is necessary to take account of the enthalpies of vibration, rotation and translation and the vibrational zero point energy. These can be induced by making empirical corrections (group or bond contributions), or by statistical mechanics. The latter route is cumbersome and not used here. Instead the group increment scheme is followed which, apart from being easier to use in practice, partially compensates within itself for small errors which might be found in the force field. It regards all structural units of a given type as contributing equally to the overall heat of formation of a molecule, irrespective of its structure. This heat is then simply the sum of all the appropriate enthalpy increments added to the V_s. The increments were themselves obtained[29] by a least squares process[30] from the experimental enthalpies and steric energies of a number of structures.

One feature indicated by the statistical mechanical approach

TABLE 1.

CONFMN.	TYPE	SYMMETRY	V_s	ΔV_s*
1	[12323]	C_1	12.67	0.0
2	[335]	C_1	13.17	0.49
3	[12314]	C_1	13.32	0.64
4	[13223]	C_2	13.50	0.83
5	$[335]_2$	C_2	14.20	1.52
6	[334]	C_2	14.32	1.64
7	$[335]_3$	C_1	14.32	1.64
8	[11324]	C_1	14.66	1.99
9	[22223]	C_2	14.98	2.30
10	[245]	C_1	15.27	2.59
11	$[13223]_2$	C_1	16.30	3.62
12	$[344]_2$	C_1	17.63	4.95
13	[12233]	C_1	19.87	7.19
14	$[245]_2$	C_1	23.16	10.48

* ΔV_s with respect to the calculated GMEC. Both V_s and ΔV_s given in kcal $mole^{-1}$.

is that since the primary contributions to the enthalpy of a molecule at 298K, namely the zero point energy, and the vibrational term, are so very similar for different conformations of that molecule, steric energy differences effectively reflect conformational energy differences. Finally, both methods neglect the fact that in the case of a molecule which is free to flex, the observed heat of formation is taken over all conformations present in the Boltzmann distribution.

It is important to remember that care should be taken when equating differences in steric energy, differences in enthalpy and differences in free energy. Energy is more intuitively convenient while enthalpy is more experimentally and thermodynamically convenient and they are interrelated by $P\Delta V$ terms, $\Delta H = \Delta E + P\Delta V$. Usually the errors in these terms are small under the conditions of interest i.e. 298K and 1 atmos. pressure.

Free energy is the thermodynamic variable which determines relative stability: $\Delta G = \Delta H - T\Delta S = -RT\ln K$, where ΔH is the enthalpy change and K is the equilibrium constant. From this equation, it is evident that the free energy is composed of an enthalpy term as well as an entropy term. The enthalpy change is essentially temperature independent whereas increasing the temperature increases the entropy term. In most cases, near ambient temperatures, the enthalpy term dominates. As such it is usually safe to assume tacitly that information about ΔH is conceptually equivalent to that about ΔG.

The MM calculations indicate that cycloundecane at room temperature is probably a mixture of several conformations and although at low temperatures there may be fewer components present there is still a mixture. Evidence to support this has come from NMR investigations of cycloundecane[31,32]: the 251-MHz ^{1}H and 63.1-MHz ^{13}C NMR spectra for cycloundecane from -5° to -170° C have been reported. The ^{1}H NMR spectrum consists of a single

absorption above -140°C (approximately). Below this temperature the resonance line broadens and at -152°C the line shape is approximately Lorentzian with a width of ca. 50 Hz. At -164°C the spectrum consists of a relatively sharp absorption (width ca. 50 Hz) on top of an unsymmetrical broad base (width ca. 200 Hz.). The ^{13}C NMR spectrum of cycloundecane consists of a single relatively sharp line above about -140°C. Below this temperature the resonance line broadens appreciably, reaching maximum broadening (width ca. 200 Hz) at about -157°C and then sharpens again (width ca. 125 Hz) with no observable new peaks at -164°C. This behaviour is indicative of exchange between two conformations with rather different populations.

Low temperature NMR spectra provide several pieces of information. If the temperature is sufficiently low, the rates of conformational interconversions may become much lower than the rate of the nuclear transition observed, thus, there is separation of one peak into two or more peaks. The ratio of the peak areas gives the ratio of the conformers present and an estimate of the conformational free energy. An additional useful piece of information can also be obtained from low temperature NMR spectra: if there are two or more conformations in equilibrium, the compound will show a low temperature spectrum which is really the separate spectra of the conformations superimposed, and an high temperature spectrum which is a single spectrum of an averaged conformation. The barriers to interconversion can be calculated from a knowledge of the coalescence temperature, which can be estimated by observation of the transition from the low temperature spectrum to the high temperature spectrum. The NMR spectral studies on cycloundecane indicate separation of two conformations at, or below, -140°C in the ratio (85-70)% : (15-30)% with a free energy difference of between 0.2 and 0.4 kcal mole^{-1}. This is in good agreement with the force field calculations which show the [12323] and [335] conformations to have a V_s difference of 0.49 kcal mole^{-1}.

Anet[33] et al interpret these results to mean that the major

conformation is the [335] and the minor conformation is the [12323] which they calculate to have the same V_s value. This conflicts with the present results which predict the major conformer to be the [12323] and the minor one, the [335]. Both interpretations are feasible as the NMR spectra are too complex to analyse completely.

Force field calculations have been performed on various conformations of cycloundecane by other workers[10,12,24,33] and these calculated structures have comparable conformations to some calculated here as shown in Table 2. The most recent of these MM calculations has been carried out by Anet and Rawdah[33] who predict the existence of six low-energy conformers (as opposed to the ten calculated here) differing in V_s by 3 kcal $mole^{-1}$ or less. Table 3 records the energy contributions to the total V_s for these six conformations as calculated by Anet and Rawdah in comparison to the results of the present study.

Correlation between TAs is good, as indicated in Table 2, with deviations of within $\pm 4^{\circ}$ for Anet's results and the present study. However, the calculated strain energies for these two studies differ by $\pm$ 4.5 kcal $mole^{-1}$. Anet uses the consistent force field of Boyd[34] (BFF) as opposed to the WBFF[22] used here. The BFF relies heavily on vibrational frequencies to ensure a satisfactory excess of observed over calculated force constants and this has been found to be at the expense of accuracy in the thermodynamic data[35]. The WBFF, however, was parameterised by trial and error methods and was based on enthalpy and structural data only with neglect of vibrational frequencies for thermodynamic data. Another area of disagreement between the two force fields is in the treatment of the various non-bonded interactions (H....H, C....H and C....C). The BFF has an "harder" H....H potential[29] i.e. at short H....H distances (with r_{HH} ca. 2 Å) the H....H potential increases more rapidly as the r_{HH} distance decreases. One consequence of employing "hard" H....H potentials is that bond lengths may be overestimated as

TABLE 2

CONFMN.	REFERENCE	11 RING TAs. (°)										
[12323]	*	-163	93	-81	128	-68	-75	164	-57	-69	76	64
	Anet[33]	-164	91	-80	128	-68	-75	165	-58	-67	75	65
	Dale[24]	-170	110	-80	130	-80	-60	170	-60	-80	85	55
[335]	*	-158	62	62	-137	65	62	-171	64	57	-98	123
	Anet	-159	60	62	-138	66	61	-172	66	55	-97	126
[12314]	*	86	-127	71	82	-167	94	-68	88	-156	154	-83
	Anet	86	-129	70	82	-168	92	-65	86	-160	153	-79
	Engler[12]	88	-128	68	82	-166	90	-66	86	-159	149	-78
[13223]	*	71	80	-71	-71	80	71	-162	95	-62	95	-162
	Anet	71	80	-70	-70	80	71	-164	94	-60	94	-164
	Dale	55	85	-80	-80	85	55	-170	105	-55	105	-170
[344]	*	59	-171	59	55	-117	146	-67	-67	146	-117	55
	Anet	59	-171	59	55	-120	147	-65	-65	147	-120	55
[245]	*	156	-65	-79	60	54	-150	159	-54	-56	108	-105
	Anet	158	-65	-77	57	54	-152	161	-53	-53	106	-106
	Dale	160	-55	-85	75	50	-160	165	-60	-40	115	-135

* Results from the present study.

TABLE 3. : All energy values given in kcal $mole^{-1}$.

CONFMN.	REFERENCE	V_b	V_a	V_w	V_r	V_s	ΔV_s
[12323]	*	0.61	4.53	4.39	3.14	12.67	0.0[a]
	Anet[33]	0.83	4.21	5.53	5.63	16.2	0.0[b]
	Dale[24]					16.1	0.0[c]
[335]	*	0.62	3.62	5.44	3.49	13.17	0.49[a]
	Anet	0.80	3.13	6.42	5.86	16.2	0.0[b]
[12314]	*	0.55	3.35	6.60	2.82	13.32	0.64[a]
	Anet	0.77	2.83	8.38	5.37	17.4	1.2[b]
	Engler[12]					15.32	0.0[d]
[13223]	*	0.63	5.87	3.99	3.01	13.51	0.83[a]
	Anet	0.89	5.75	5.34	5.70	17.7	1.5[b]
	Dale					17.0	0.9[c]
[344]	*	0.62	3.45	6.50	3.74	14.32	1.64[a]
	Anet	0.80	2.90	7.52	6.18	17.4	1.2[b]
[245]	*	0.71	5.08	5.49	3.99	15.27	2.59[a]
	Anet	0.94	4.56	6.83	6.57	18.9	2.7[b]
	Dale					18.7	2.6[c]

* Results from present study.

a : w.r.t. GMEC [12323]*

b : w.r.t. Anet's GMEC

c : w.r.t. Dale's GMEC

d : w.r.t. Engler's GMEC

seen in several calculations[36] involving the BFF. It has been observed[29] that an acceptable balance of forces between the different functions in the force field must be employed otherwise serious consequences can result - incorrect geometrical parameters, heats of formation, conformational energies (and hence minimum energy conformations) and incorrect interpretation of trends in molecular properties. The WBFF has been extensively tested and the average absolute differences between the observed and calculated values of 93 geometric parameters amounts to 0.009 Å, 0.6° and 0.9° in bond lengths, bond angles and torsion angles, respectively. The corresponding figures for enthalpies of formation/hydrogenation of 60 associated hydrocarbons is 0.55 kcal $mole^{-1}$. An interesting correlation in Table 3 is that both studies predict conformer 3 i.e. the [12314], to have the lowest bond energy, angle energy and van der Waals interaction energy while having the highest torsional strain of the recorded conformations. Similarly, conformer 4, the [13223] is calculated to have the highest valence angle energy and the lowest torsional energy while conformer 10, the [245] has the highest bond strain and van der Waals interaction energy of these six conformations, in both studies.

Tables 2 and 3 also include conformational results for cycloundecane from other workers. Dale employs a semi-quantitave method for calculation of the conformational energy of cycloalkanes. Such a method employs considerable approximations and selection of conformational candidates by observation of Fieser-Dreiding molecular models is of dubious utility when there are a large number of low-energy conformational possibilities. However, there is general agreement between the [12323], the [13223] and the [245] conformations obtained here and those reported by Dale. The TAs agree generally to within $\pm$ 20° and although the strain energies calculated by Dale and Anet agree to within $\pm$ 1 kcal $mole^{-1}$ this appears to be coincidental rather than correlative. Several discrepancies arise between Dale's results and those of the present study: he predicts a [344] conformation to be the GMEC which is calculated here to be a

symmetrical transition state by the appearance of 3N-7 positive eigenvalues for the matrix of second derivatives of V_s. Dale suggests that although the [12323] has lowest V_s, it is an ill-defined state intermediate in character between a triangular and quinquangular structure, whereas it is predicted to be the GMEC in the present study. The symmetrical [335] conformation considered by Dale corresponds to a maximum energy conformation comparable to one predicted both by the present work and by Anet.

Schleyer[12] et al examined only two conformations of cycloundecane, one of which corresponds to an energy minimum, the [12314], calculated to have a strain energy of 15.2 kcal $mole^{-1}$. The other structure is the symmetrical [344] conformer also found by Dale, Anet and Bixon and Lifson[15] which they suggest is an energy minimum but which is calculated here to be an energy maximum. Anet suggested that this conformation lies on a relatively flat-bottomed energy well whereas the present analysis prefers a flat-topped energy hump. Schleyer's force field, like the WBFF, is parameterised using only structural and enthalpy data but employs H....H potentials which overestimate the repulsive term i.e. the H....H potentials are too hard, which leads to errors in the results.

The present work predicts the existence of 10 energy maxima - some of which are very similar in conformation and energy suggesting broad maxima at these points - which leaves 5 unique transitional states. All transitional conformers are drawn in Figures 2.15 - 2.24 and can be separated into the 5 unique states as follows:

1_T Figures 2.15 - 2.17
2_T Figure 2.18
3_T Figures 2.19 - 2.22
4_T Figure 2.23
5_T Figure 2.24

Their TAs are recorded in Table 4 with the subscript T indicating they are energy maxima - averaged values are recorded for 1_T and 3_T.

The first three conformations have approximate C_2 symmetry while 4_T and 5_T have C_1 symmetry. Included in Table 4 are the corresponding results from other workers while Table 5 records the energy contributions of each (again with averaged values for 1_T and 3_T). A scheme for the interconversions of cycloundecane conformations has been proposed by Dale[24,25] and supported by Anet[33]. The semi-quantitative calculations of Dale predict the conformational energy of the cycloalkanes by the relationship between TAs and the corresponding torsional energy in the potential energy curve for internal rotation about the central bond in butane. Angle strain, therefore, is neglected. Anet and coworkers used Dale's scheme as a basis for iterative force field calculations on the transition states for the interconversions. It is not surprising, therefore, that Anet's results support those of Dale. The energy maxima predicted in this study do not have analogous conformations in Dale's (or Anet's) scheme and are of much lower V_s than those calculated by either Dale or Anet. However, since transition states are by their nature unobservable species there are no structural or spectroscopic data with which to check the calculated results.

The only strain-free saturated carbon skeletons are those which can be derived from the diamond lattice[37]. This means that only even-membered carbon rings C_6 and higher can have skeletons without torsional strain, but the 8-, 10- and 12-membered rings are strained because of repulsion between hydrogen atoms pointing in towards the centre of the ring. The odd-membered medium rings possess inherent strain which can be distributed in various ways without, or with only little, difference in energy. The undetermined nature of odd-membered rings is reflected in the crystal structure of cyclononylamine hydrogen bromide[38] which contains two similar conformers for the nine-membered ring, which differ in the position of attachment of

TABLE 4.

CONFMN.	REFERENCE	11 RING TAs (°)										
1^T	*	103	-130	72	72	-153	57	56	-157	72	72	-125
	Dale[24]	130	-135	65	60	-165	70	70	-165	60	65	-135
	Anet[33]	111	-132	71	68	-155	60	60	-155	68	71	-132
2^T	*	167	-117	67	-101	152	-67	-69	159	-101	63	-105
3^T	*	142	-141	60	61	-156	56	55	-142	150	-51	-52
	Dale	150	-150	70	50	-155	50	70	-150	150	-50	-50
	Anet	148	-147	57	58	-155	58	57	-147	148	-48	-48
	Engler[12]	142	-152	58	58	-144	56	56	-153	145	-43	-44
	Bixon[10]	147	-164	59	57	-145	57	56	-165	144	-30	-47
4^T	*	153	-124	80	-88	144	-66	-92	69	84	-69	-67
5^T	*	-92	96	-79	-69	131	-77	125	-56	-68	-2	129

TABLE 5. : All energy values are given in kcal $mole^{-1}$.

CONFMN.	REFERENCE	V_b	V_a	V_w	V_r	V_s	ΔV_s
1_T	*	0.57	2.99	7.06	3.56	14.17	1.50[a]
	Dale[24]					16.6	0.5[b]
	Anet[33]	0.82	2.20	0.50	6.59	18.2	2.0[c]
2_T	*	0.51	2.99	2.87	7.85	14.23	1.56[a]
3_T	*	0.78	3.41	5.77	5.13	15.09	2.42[a]
	Dale					16.4	0.3[b]
	Anet	0.93	2.88	6.51	7.51	17.8	1.6[c]
	Engler[12]					18.07	2.75[d]
	Bixon[10]					10.77	-
4_T	*	0.61	4.89	6.54	3.34	15.38	2.71[a]
5_T	*	0.72	7.85	9.49	4.07	22.13	9.45[a]

* Results from the present study

a : w.r.t. [12323] GMEC *

b : w.r.t. Dale's GMEC

c : w.r.t. Anet's GMEC

d : w.r.t. Engler's GMEC

the amine function. The result of the structure analysis of the triclinic modification of the dihydrochloride of trans-1,6-diaminocyclodecane[39] reveals that there are two groups of hydrogen atoms, three above the ring and three below, which are subjected to an high degree of steric compression and thus direct confirmation is provided of the reality of transannular strain. Most surprisingly, however, the structure shows practically no Pitzer strain, this favourable arrangement being accommodated by deformation of the C-C-C ring angles to an expanded average value of 117°. A similar transannular compression of hydrogen atoms is revealed in cyclononyl ammonium bromide which has a much less regular shape for the nine-membered ring. Once again the C-C-C angles possess an expanded value averaging 117°. Unlike those in the ten-membered ring, the partial conformations around the nine-membered ring are not all favourably staggered and thus Pitzer strain does make some contribution to the high energy content of the latter. As mentioned previously, the immediate molecular environment of a ring methylene group may be defined by its relationship to its two flanking pairs of methylene groups[23]. Examples of such five-carbon conformations were shown previously and are referred to as types I to IV. Conformation I occurs six times in the chair form of cyclohexane and conformation IV is the familiar zig-zag arrangement of the paraffins. In the medium-sized rings, types II and III play an important role and an analysis of the predicted low-energy conformations of cycloundecane in terms of types I to IV is given in Table 6.

Comparison of conformers 1 and 2 reveals a common arrangement over nine ring atoms as indicated below:

[12323]	164	-57	-69	76	64	-163	93	-81	128	-68	-75
[335]	171	-64	-57	98	-123	158	-62	-62	137	-65	-62

Correlation of the ring TAs° for the GMEC [12323] and next lowest energy conformer [335] of cycloundecane.

TABLE 6 : Analysis of Partial Confmns.
(Types I to IV) present in Cyloundecanes.

CONFMN.	I	II	III	IV
1	2	3	6	0
2	1	3	6	1
3	3	1	6	1
4	4	3	4	0
5	4	1	6	0
6	2	3	6	0
7	2	2	6	1
8	2	1	6	2
9	4	5	2	0
10	3	3	4	0
11	4	3	4	0
12	1	3	6	1
13	2	5	4	0
14	4	5	2	0

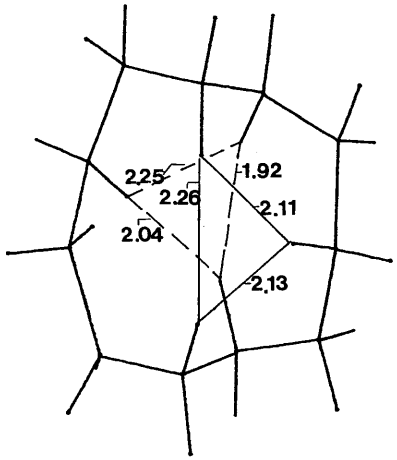
The difference between these conformers results in conformer 1 having a more favourable type I arrangement as opposed to a type IV - this is reflected in torsional strain energies of the two conformations. Conformer 1 has some obviously unfavourable features: two triangles of hydrogen atoms above and below the central plane of the ring are squeezed tightly together to give non-bonded H....H contacts in the range 1.92 - 2.26 Å which are similar to those found in cyclononyl ammonium bromide and 1,6-diaminocyclodecane. Some of the valence angles in [12323] are widened to 117° instead of the normal 112.5° found in unstrained polymethylene chains. This suggests there will be decided Baeyer strain and non-bonded interaction energy which is, indeed, the case.

Conformer 2 has, in Dale nomenclature, fewer corners than conformer 1 which, in turn, means that it will have more intra-annular H....H interactions. Figure 2.25 is suggestive as to just which hydrogens are involved in transannular interactions in conformers 1 to 4. It is found that conformer 2 has reduced the Baeyer strain with respect to conformer 1 at the expense of a considerable amount of Pitzer strain. Some of the C-C-C angles are widened resulting in an average value for these ring angles of 115°.

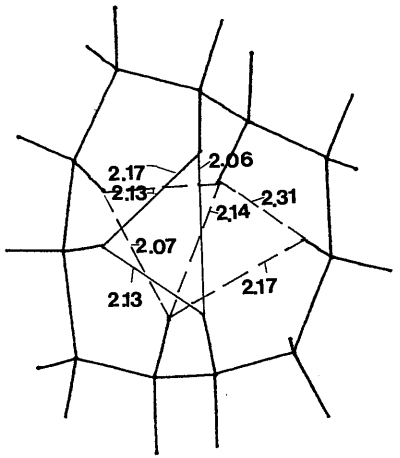
The components of the total V_s for each of the 14 low-energy conformers of cycloundecane are recorded in Table 7: it is readily seen that in all cases the bond strain is less than, or equal to 5% of the total V_s and the van der Waals interaction energy accounts for 20-25% of V_s. The remaining 70-75% is apportioned between Baeyer and Pitzer strain.

Both Hendrickson[9] and Allinger[41] have studied the trends in energy components of V_s in medium rings: Hendrickson suggests that torsional strain increases to a peak for cyclononane, Baeyer strain increases and decreases in a zig-zag fashion from even rings to odd rings and non-bonded interaction energy increases to a peak at cyclodecane. Allinger, however, calculates the major

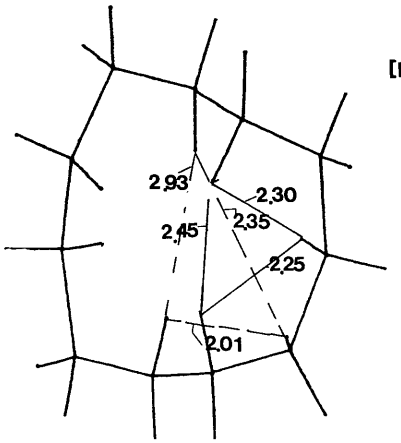
FIG. 2.25 Transannular H···H interactions (distances in Å)
V_S in kcal.mole^{-1}



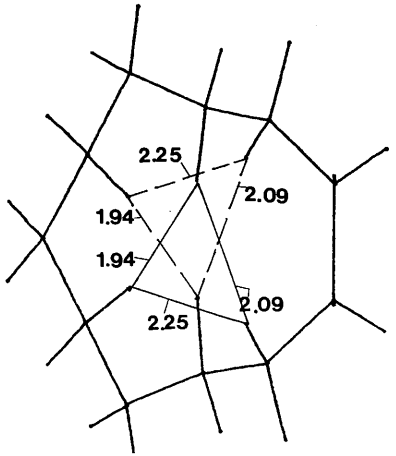
[12323]
V_S = 12.67



[335]
V_S = 13.17



[12314]
V_S = 13.32



[13223]
V_S = 13.50

TABLE 7. : All energy values given in kcal $mole^{-1}$.

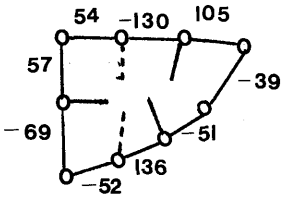
CONFMN.	V_l	V_r	V_a	V_w	V_s
1	0.61	3.14	4.53	4.39	12.67
2	0.62	3.49	3.62	5.44	13.17
3	0.55	2.82	3.35	6.60	13.32
4	0.63	3.01	5.87	3.99	13.50
5	0.51	2.98	2.87	7.83	14.20
6	0.62	3.74	3.45	6.50	14.32
7	0.58	3.14	3.58	7.02	14.32
8	0.58	3.28	3.40	7.40	14.66
9	0.74	3.49	8.30	2.44	14.97
10	0.71	3.99	5.08	5.50	15.27
11	0.62	3.28	5.44	6.95	16.30
12	0.78	4.53	5.53	6.79	17.63
13	0.84	4.54	8.69	5.80	19.87
14	0.88	4.57	11.34	6.36	23.16

contributions to the strain inherent in these medium rings to be a concomitant increase in van der Waals and and bending energies with ring size. It has been shown[29] that Allinger's and Hendrickson's force fields employ non-bonded H....H potentials which differ from the WBFF potentials: the former uses unrealistically hard potentials resulting in overestimated non-bonded energy and underestimated Pitzer strain. The latter uses non-bonded H....H potentials which are almost as soft as those used here and it is suggested that the predicted trends in V_s components by Hendrickson are more readily acceptable on this basis.

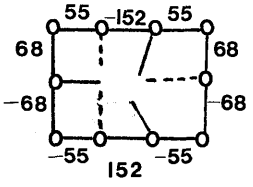
The GMEC [12323] of cycloundecane bears a close resemblance to low-energy conformations of cyclononane and cyclodecane (see Figure 2.26). The [2323] C_{10} conformation has been established as the preferred low-energy one by MM calculations[29] and from neutron[40] and x-ray diffraction[13] studies. The [234] C_9 conformation is a low-energy conformer which has been observed in an x-ray study of 4,4,7,7-tetramethylcyclononanone[42] and has also been proposed for 2,3,4-trioxacyclononane[43] but which is predicted[44] to be slightly higher in energy than other low-energy cyclononane conformations as a result of its considerable transannular non-bonded repulsions.

The H....H transannular interactions have been included in the representations in Figure 2.26: two triangles of H....H contacts are observed above and below the planes of the ring in the C_{10} and C_{11} arrangements but only one triangle is observed in C_9 as the other triangle cannot be completed since there is no carbon in the required section of the ring. It is at this section that an extra carbon is inserted to form the C_{10} conformation and it is here that the two arrangements (C_9 and C_{10}) show variation.

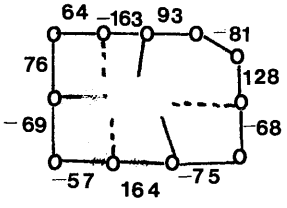
The cyclodecane conformer is calculated[29] to have a V_s of 14.10 kcal $mole^{-1}$ i.e. 1.42 kcal $mole^{-1}$ higher in energy than the



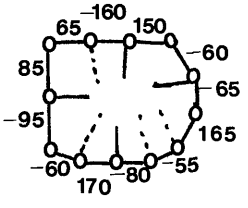
Cyclononane [234]



Cyclodecane [2323]



Cycloundecane [12323]



Cyclododecane [2334]

FIG. 2.26

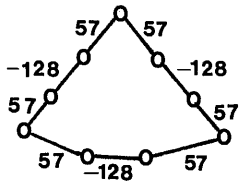
represented cycloundecane. In C_{10} the six transannular H....H distances are less than, or equal to 2 Å whereas in C_{11} only four of these H....H contacts are this short. The WBFF predicts that the energy per H....H interaction at 2 Å is 0.69 kcal $mole^{-1}$ thus the C_{10} ring would have a transannular H....H energy of ca. 4.14 kcal $mole^{-1}$ for these six contacts whereas the C_{11} ring has a calculated energy of 2.75 kcal $mole^{-1}$. The increase in V_s of 1.42 kcal $mole^{-1}$ for C_{10} with respect to C_{11} can be explained largely on the basis of the increased H....H transannular contribution. It is not remiss, therefore, to observe a maximum for the van der Waals energy in cyclodecane with respect to the other medium rings.

Observation of the TAs for all three conformations in Figure 2.26 reveals that cyclodecane has two TAs of ca. 150° and eight in the range 50-70° i.e. small variations from the ideal values of 180° and 60°. Cyclononane and cycloundecane show greater variations from ideal values and it is expected that the C_{10} conformation has less Pitzer strain than either the C_9 or C_{11} conformers. The [2323] cyclodecane conformation is of the diamond lattice type[37] which suggests it should have small torsional strain: the usefulness of the diamond lattice in deriving stable conformations was first pointed out by J.C.Speakman[45].

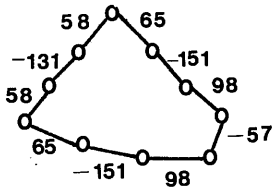
Thus, as Dale has pointed out, the [12323] is derivable from the [2323] conformation of cyclodecane by ring expansion. It is suggested here that this [2323] conformation is derived from ring expansion of the [234] cyclononane conformation. Included in Figure 2.26 is a [2334] conformation of cyclododecane which bears a close resemblance to the other, recorded conformations . This conformer is not the preferred low-energy one but has been calculated to be of next lowest energy by Dale[25] and by Anet et al[46].

The next lowest energy conformer of cycloundecane, the [335], is derivable from the square [3333] conformation of

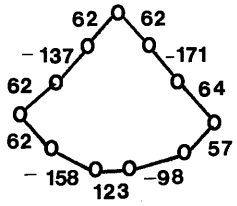
cyclododecane by ring contraction. Both are represented in Figure 2.27 together with comparable C_9 and C_{10} conformers. This square [3333] C_{12} conformation, although not of the diamond lattice type, is distinctly preferred for cyclododecane according to all strain energy calculations[24] and is also the one observed in the solid[47] and in solution[46]. The cyclodecane conformer, the[1333], is a low-energy one although it is not the GMEC[29]. For cyclononane there appears to be a serious discrepancy between results of experimental structure analysis[38] and of MM calculations[9,10,12,24,44,48] : the observed conformation,a [245], is not the one favoured by the calculations, a [333]. Anet and coworkers suggest that entropy effects on the conformational equilibria are substantial because of the high symmetry and rigidity of the [333] conformation and, as a result, the [333], which makes up ca. 95% of cyclononane at -173°C, has a population of only 40% at room temperature.



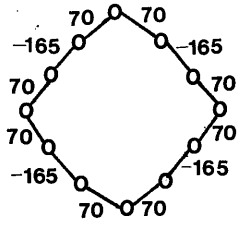
Cyclononane [333]



Cyclodecane [1333]



Cycloundecane [335]



Cyclododecane [3333]

FIG. 2.27

2.3 THE EFFECT OF INTRODUCING A DOUBLE BOND INTO CYCLOUNDECANES.

In order to explain the varying reaction rates in chemical reactions of cyclic systems H.C.Brown proposed the I-strain theory[49] in which I-strain is defined as the "change in internal strain which results from change in coordination number of a ring atom involved in a chemical reaction"[50]. This theory suggests that the differences in reaction rates for various cyclic compounds depend on the relief or increase in angle strain and / or transannular strain during the reaction.

For the medium-sized rings, substitution of a trigonal sp^2 atom for a tetrahedral sp^3 atom relieves I-strain by removing some transannular interactions and by increasing a C-C-C bond angle. Consequently, reactions that proceed from a species consisting entirely of sp^3 atoms to one in which an sp^2 atom is present occur readily in medium ring compounds. The solvolysis of cycloalkyl bromides and tosylates, the dissociation of cycloalkanone cyanohydrins and the dissociation of azacycloalkane conjugate acids provide some examples[51]. Some irregularities are observed which probably indicate that effects other than I-strain may be important in certain cases, but the I-strain concept is a useful approach as a first approximation when more detailed information is not available.

The introduction of one or more double bonds into a cyclic system leads to interesting structural consequences: firstly, as the barrier to rotation about a C=C double bond is much larger than about a C-C single bond, the cis and trans arrangements will be virtually coplanar with TAs of 0° and 180° respectively. Secondly, the preferred C-C-C=C TA about a single bond adjacent to a double bond is close to 120° , corresponding to eclipsing of one of the hydrogen atoms of the α-methylene group with the double bond.

Dale[52] has stated that in rings containing one double bond the constraints are such that no absolutely strain-free

conformation of the saturated chain can be achieved. He interprets the low melting points of cyclic mono- and di-olefins as evidence of their conformational instability.

The relative stabilities of cis and trans cycloolefins have been estimated from their heats of hydrogenation which also give an idea of their strain relative to the corresponding cycloalkane. Table 8 shows that, for example, the trans cycloolefins are more strained than the cis isomers in 8-, 9- and 10-membered [53] rings. The trans olefins for larger rings are slightly more stable than the cis isomers, as shown by equilibration studies[54] - the results of which are are also included in Table 8.

TABLE 8 : Heat of hydrogenation, $-\Delta H$, (kcal $mole^{-1}$) of cycloalkanes in acetic acid at 25°C.

Isomerisation of cycloalkenes, trans -> cis, at 100° C : $\Delta G, \Delta H$ (kcal $mole^{-1}$), ΔS (e.u.)

	HEAT OF HYDROGn.		ISOMERISATION		
Ring Size (n)	$-\Delta H_{trans}$	$-\Delta H_{cis}$	ΔG	ΔH	ΔS
6	-	27.1			
7	-	25.9			
8	32.2	23.0			
9	26.5	23.6	-4.04	-2.9	3.0
10	24.0	20.7	-1.86	-3.6	-4.7
11	-	-	0.67	0.1	-1.5
12	-	-	0.49	-0.4	-2.4

These results have been confirmed by MM calculations[29].

It was decided to investigate some of the low-energy conformations of cycloundecenes. Initial structures were obtained by conversion of a single bond to a double bond for each of the low-energy conformers of cycloundecane via GUCGS. In all cases, the single bond with the largest TA was converted into a

trans double bond. This does not, therefore, represent a systematic quest for all the low-energy conformers of trans cycloundecenes.

All starting geometries were optimised by a two stage NR energy minimisation algorithm and were terminated when the elements of the first derivatives of energy with respect to the coordinates were less than 10^{-5} kcal $mole^{-1}$ $Å^{-1}$.

The same procedure was applied to the ten transition state conformers of cycloundecane and subsequent optimisation of these starting structures resulted in 9 energy minima and 1 energy maximum. MM calculations on the 24 initial structures produced 15 unique low-energy conformers whose TAs and V_s values are recorded in Table 9. This also includes the name of the cycloundecane(s) from which a given cycloundecene was derived.

The calculated lowest-energy conformer of cycloundecene was derived from cycloundecane 5. This latter conformation represented the one with highest torsional strain in the cycloundecanes as some of its TAs were far removed from the preferred sc and ap values: the TAs of the bonds on either side of the proposed double bond were nearer to 120^{o} than 90^{o} and this is an advantageous factor in forming the double bond. Another feature favouring the cycloundecene is the removal of two major H....H interactions within the ring as compared to the saturated cycloalkane. In moving from the cycloundecane to the cycloundecene Baeyer, Pitzer and van der Waals strain have all been reduced by over 40% of their original values. In this case changes of bond hybridisation have resulted in favourable changes in angle, torsion and transannular strain. ORTEP representations of the 4 lowest-energy conformations are given in Figures 2.28 - 2.31.

TABLE 9

CYEN	CYAN[a]	V_s[b]	11 RING TAs[c] (°)										
1	5, 2_T	7.66	-179	115	-59	92	-155	74	74	-155	92	-59	115
2	8	8.80	-179	115	-69	78	-125	170	-69	-69	116	-72	112
3	4, 4_T	9.44	-176	104	-58	89	-159	69	90	-67	-71	69	81
4	1	10.36	177	-95	-62	116	-79	94	-172	64	72	-64	-49
5	10	10.74	176	-59	-75	52	60	-151	161	-60	-46	90	-116
6	1_T*	10.88	178	-80	-58	119	-66	-70	171	-100	83	-73	-30
7	2, 3	11.46	180	86	47	-86	127	-164	62	64	-135	65	49
8	5_T	11.71	176	-111	92	-64	-70	92	71	-149	100	-46	-61
9	7	11.73	-177	105	-76	110	-83	111	-171	100	-75	71	33
10	9	12.14	173	-73	-63	71	71	-85	-85	71	71	-63	-73
11	6, 3_T*	12.23	-180	82	44	-100	150	-75	-71	144	-111	60	39
12	11	12.81	173	-112	36	63	-153	118	-121	63	67	-76	-81
13	12	14.26	175	-58	-45	107	-151	100	-80	143	-56	-41	-38
14	13	14.90	171	-69	-54	126	-62	-87	71	91	-53	-45	-27
15	14	18.20	-172	127	-22	-74	74	81	-65	-98	45	37	33

a : cycloundecane (Cyan) from which the cycloundecene (Cyen) was derived.

b : in kcal $mole^{-1}$

c : TA in first column corresponds to that of the double bond.

* : 1_T and 3_T are averaged representations.

FIG. 228

V_s = 7.66

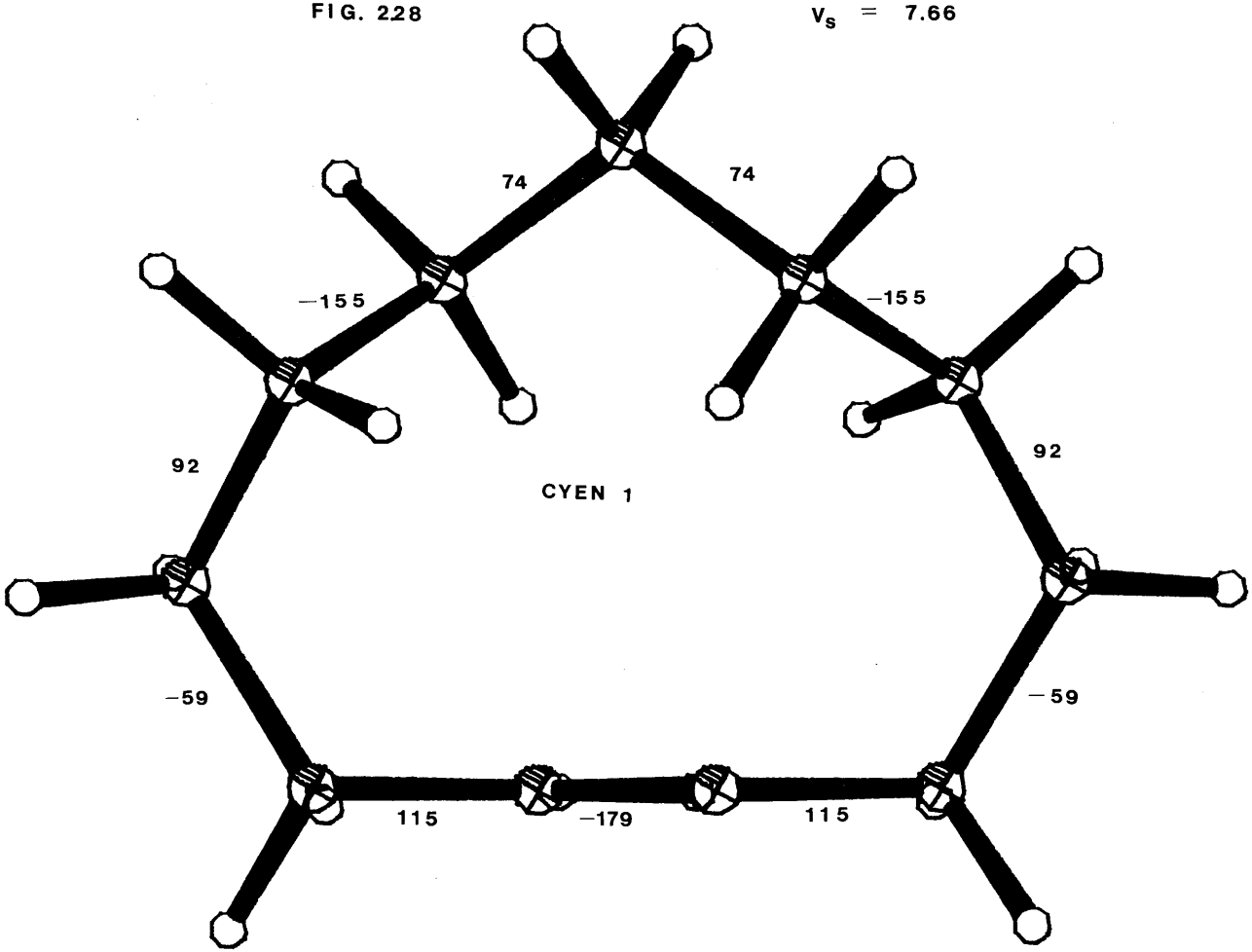
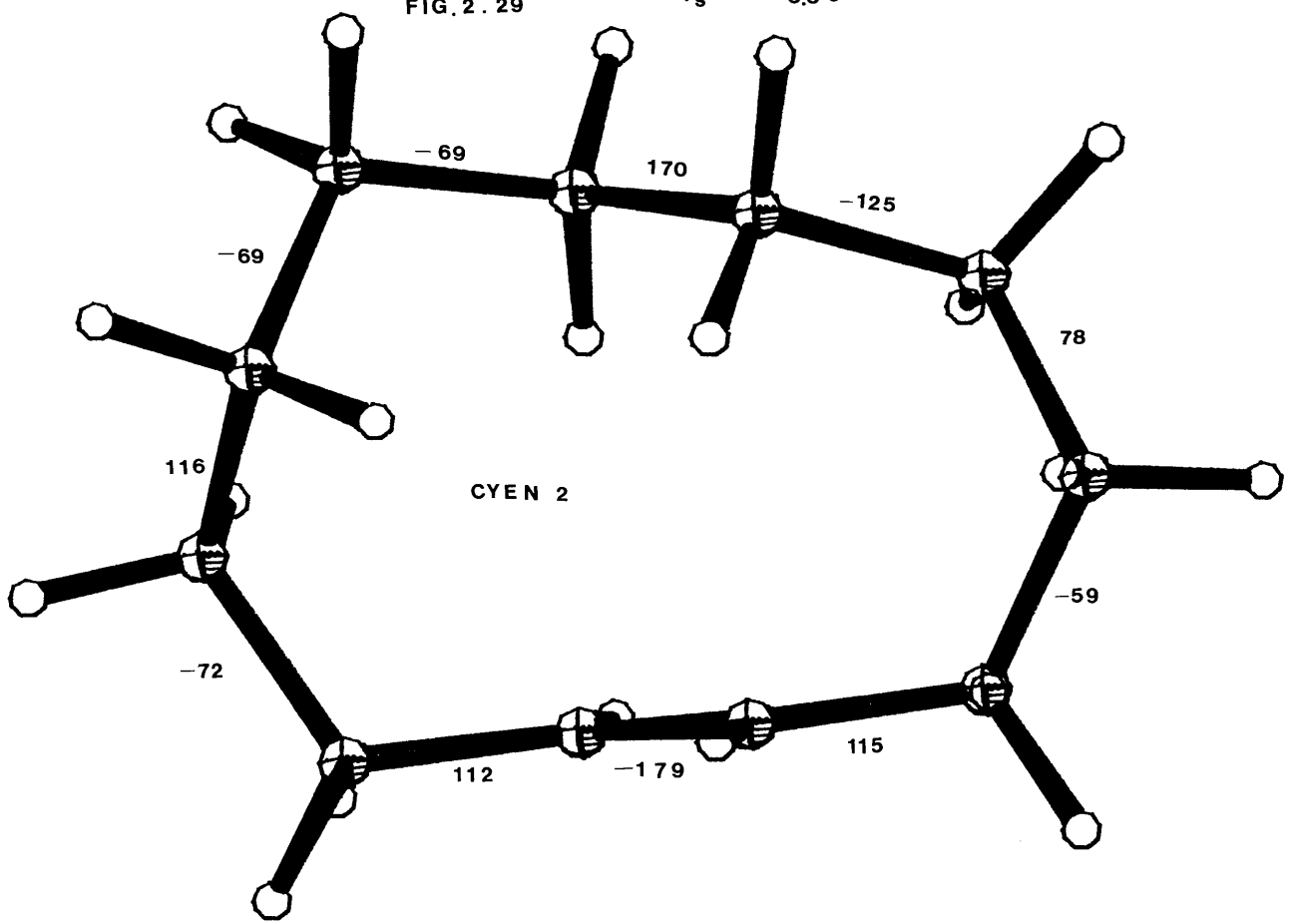


FIG. 2.29 $V_S = 8.80$



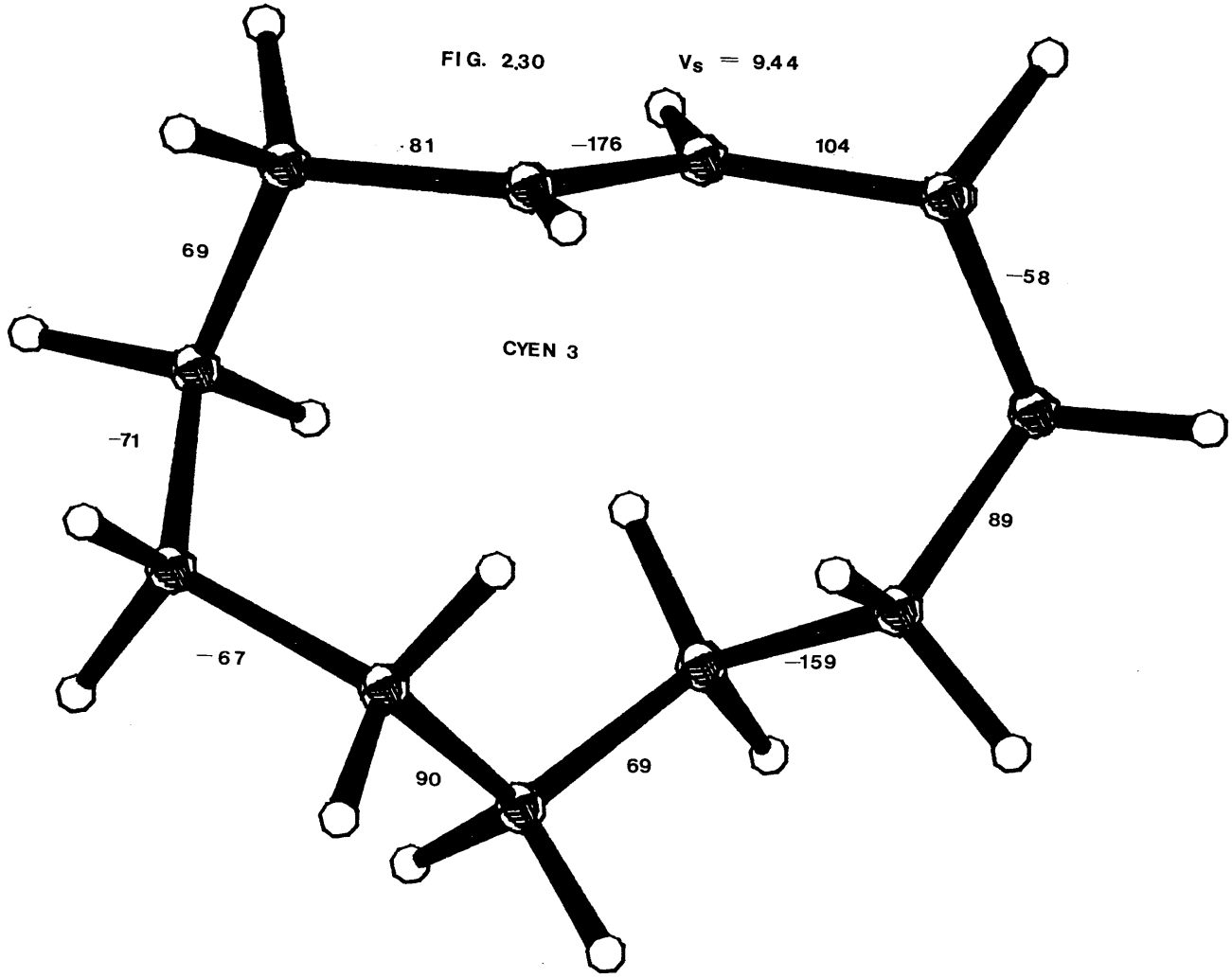


FIG. 2,30
V_S = 9.44
81
−176
104
69
−58
CYEN 3
−71
89
−67
−159
90
69

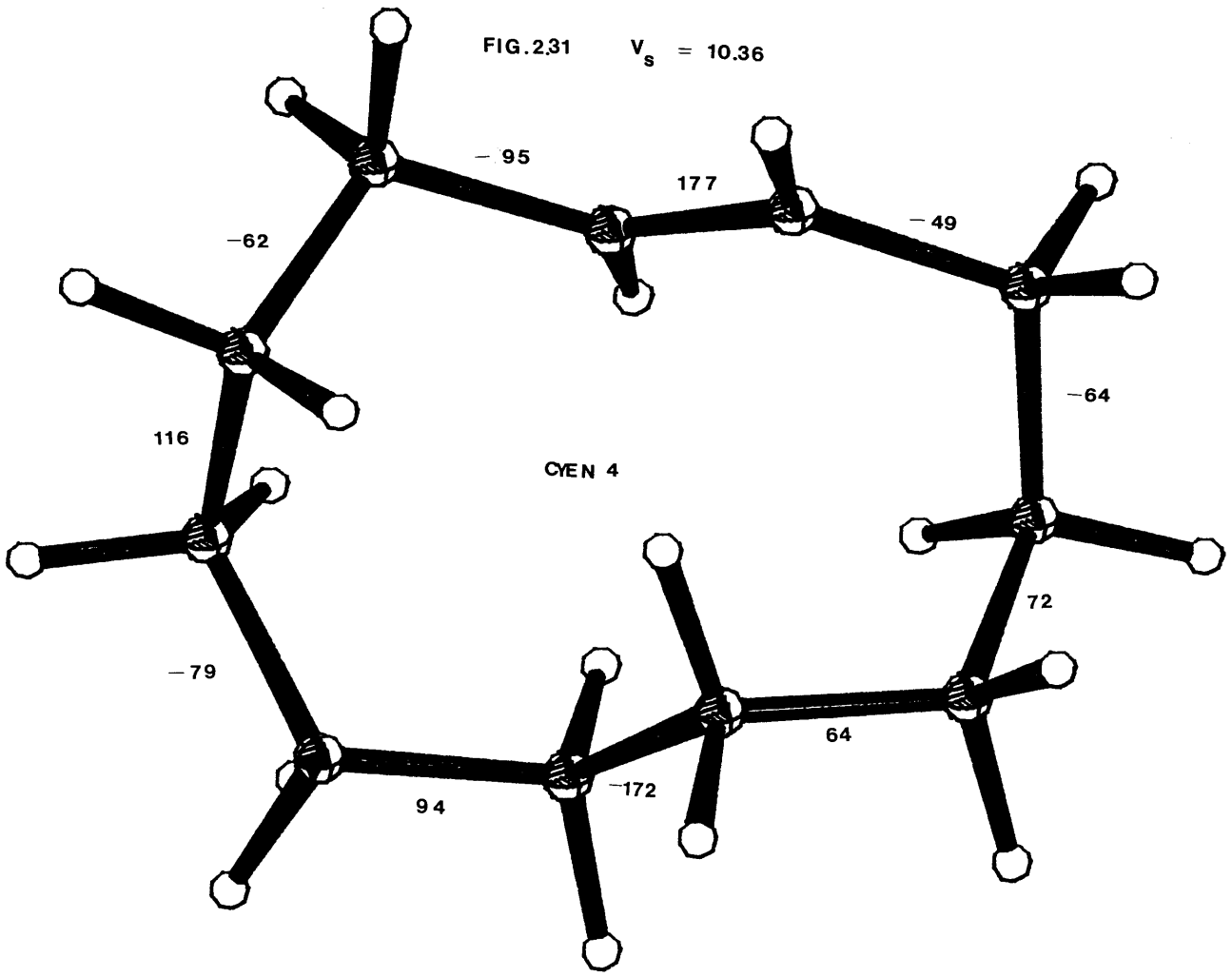


FIG. 2.31 V_s = 10.36
− 95
177
−49
−62
−64
116
CYEN 4
72
−79
64
94
−172

2.4 CORRELATION OF OBSERVED AND CALCULATED CONFORMATIONS

Prior to this study only three x-ray analyses had been reported for cycloundecane derivatives, namely cycloundecanone[55], cycloundecaneoxime[56] and cycloundecylamine hydrobromide[13]. The first two were analysed at -165°C and -160°C respectively while the x-ray analysis of the last compound has not led to a clear picture of its conformation.

The ketone exists as a [335] conformation with the carbonyl group unsymmetrically located near the middle of the long side of this triangular conformation. The oxime exists as a [12323] dimer with O-H....N′ hydrogen bonds in the range 2.62-2.81 Å. The investigation of the oxime revealed the OH group as disordered and it was calculated that in 85% of the crystals the oxygen is over C_2 whereas in 15% it is over C_{11}.

The reported geometry of cycloundecanone[55] is in good agreement with the calculated [335] form of cycloundecane - conformer 2. Corresponding TAs are indicated in Figure 2.32 in which the numbering system is that used in the x-ray analysis of the ketone. Observed and calculated interatomic distances and bond angles are given in Table 10.

Correlation between calculated and observed TAs for cycloundecane [12323] and cycloundecaneoxime[56] is given in Figure 2.33 while valence angles and interatomic distances are recorded in Table 11. The numbering system employed in Figure 2.33 and in Table 11 is that referred to in the reported structure of the oxime.

Fig. 2.32

Internal values: calc. TAs for cycloundecane conformer 2. (o)
External values: obsd. TAs for cycloundecanone[55].

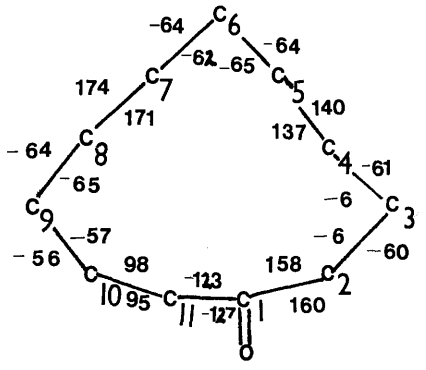


Fig. 2.33

Internal values: calc. TAs for cycloundecane GMEC. (o)
External values: obsd. TAs for cycloundecaneoxime[56].

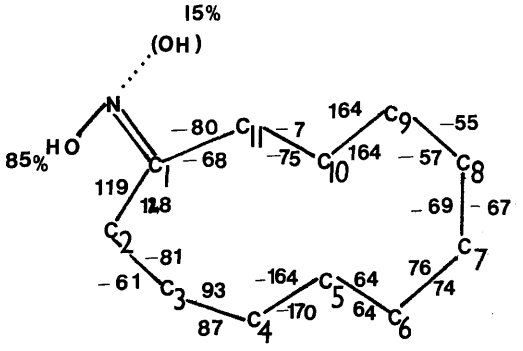


TABLE 10 : Valence angles (°) and bond lengths (Å) for Cycloundecanone[55] (I) and for Cycloundecane 2 (II).

ANGLE	I	II	LENGTH	I	II
11-1-2*	119.3	113.9	1-2*	1.515	1.530
1-2-3	114.3	113.6	2-3	1.532	1.532
2-3-4	113.8	113.5	3-4	1.528	1.535
3-4-5	115.4	115.9	4-5	1.536	1.535
4-5-6	113.8	116.6	5-6	1.540	1.531
5-6-7	114.2	114.5	6-7	1.537	1.530
6-7-8	114.0	113.7	7-8	1.523	1.534
7-8-9	115.6	115.7	8-9	1.527	1.534
8-9-10	116.0	114.2	9-10	1.522	1.533
9-10-11	114.6	114.5	10-11	1.538	1.535
10-11-1	113.9	115.7	11-1	1.516	1.530

* : numbers refer to ring carbon atoms.

TABLE 11 : Valence angles (°) and bond lengths (Å) for Cycloundecaneoxime[56] (III) and for Cycloundecane 1 (IV).

ANGLE	III	IV	LENGTH	III	IV
11-1-2	119.6	114.1	1-2	1.504	1.534
1-2-3	120.7	115.4	2-3	1.533	1.534
2-3-4	115.8	114.7	3-4	1.538	1.532
3-4-5	112.8	113.4	4-5	1.505	1.530
4-5-6	114.9	114.6	5-6	1.531	1.532
5-6-7	117.8	116.6	6-7	1.530	1.535
6-7-8	116.9	116.9	7-8	1.520	1.536
7-8-9	117.4	117.3	8-9	1.527	1.532
8-9-10	114.9	114.2	9-10	1.513	1.531
9-10-11	112.9	113.5	10-11	1.534	1.531
10-11-1	113.3	114.7	11-1	1.502	1.533

Correlation between the geometrical parameters of cycloundecaneoxime (III) and cycloundecane GMEC (IV) indicates poorer agreement than that found between cycloundecanone (I) and cycloundecane conformer 2 (II). In both comparisons there are differences around C_1 since this is an sp^2C in I and III and an sp^3C in II and IV.

The greatest differences between III and IV occur in that region of the ring in which there is substitution of a methylene group by the oxime. The reported structure also indicated the presence of disorder at this part of the compound (thermal parameters are not included in the report) due to the hydroxyl group.

Although the conformation observed for cycloundecanone in the crystal is actually the one calculated to be the second most stable, the calculated difference in energy between [12323] and [335] is small enough that the presence of substituents, or the lattice energy of the crystal, could well invert the stability order.

A strain energy minimisation calculation was performed on cycloundecanone using the WBFF[22], with additional parameters incorporated for the ketone function. (These are recorded in the appendices). The resulting structure had a calculated V_s of 11 kcal $mole^{-1}$ which is less than that calculated for either cycloundecane 1 or 2. The reduction in V_s with respect to cycloundecane 2 is due mainly to decreased Pitzer strain around the central bond of its long side i.e. where the substituent oxygen is found, by removal of hydrogens which were eclipsing ring bonds.

In cycloundecaneoxime, hydrogen bonding in the crystal structure between the substituent atom on each unit of the dimer may introduce stability into the system so that the calculated, preferred conformation is the one observed.

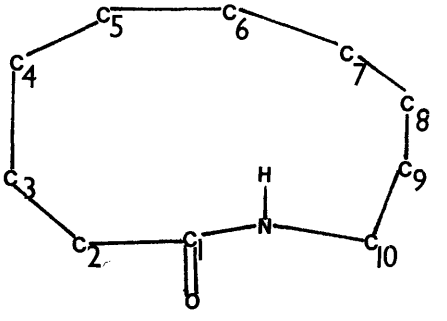
However, these x-ray studies have provided evidence of the existence of two conformers of cycloundecane which correspond to the calculated lowest energy conformers 1 and 2. Further evidence of the conformation of cycloundecanes comes from x-ray analyses of cycloundecylmethylnaphthylurethane and a cycloundecylmethyl 3,5-dinitrobenzoate which are included as part of this thesis and discussed in Chapter 6.

The replacement of a methylene group by one bivalent group to form a double bond can be regarded as a perturbation with more or less predictable consequences which occurs without significant conformational changes to the ring skeleton. Although differences arise due to variation of bond angles and bond lengths in moving from an sp^3 to an sp^2 centre it is reasonable to assume that there should be a corresponding cycloalkane structure from which the derivatives are formed. In the medium ring ketones one would expect the carbonyl group to occupy a position where transannular repulsions could be relieved i.e. a non-corner position. This is found to be the case not only in cycloundecanone but also in cyclodecanone[61] and cyclododecanone[62]. NMR spectra of cycloundecanone at low temperatures are fairly informative unlike those of cycloundecane. The CMR spectrum[57] at low temperatures shows the presence of a single CO resonance and resonances for two Cs. The proton spectrum is complex but shows clear evidence for two conformational processes with free energies of transition of 6.0 and 6.9 kcal $mole^{-1}$. The main conclusion of these results is that cycloundecanone exists predominantly in a single, unsymmetrical conformation.

Cycloundecaneoxime also has substitution at a non-corner atom which reduces the transannular repulsions with respect to cycloundecane GMEC.

The present work also introduces x-ray analyses of some unsaturated derivatives of the 11-membered ring namely, dimethyl (8′-dimethylaminonaphthyl)ammonium dihydrogen tris(cycloundec-1-

ene carboxylate) and zerumbone 2,4-dinitrophenylhydrazone which are discussed in Chapters 4 and 5 respectively. In general, experimental data for cycloundecenes that might provide corroboratory evidence for the calculated conformers are sparse and inaccurate. However, a series of crystal structural studies has been carried out for the medium ring lactams and their adducts with HCl and the structural parameters found may be compared with those calculated for the corresponding cycloolefin. The one of interest here is that of caprinolactam hemihydrochloride[61] which was prepared from cycloundecanone and which shows some order-disorder effects in its structure. However, it corresponds to a calculated cycloundecene derived from cycloundecane 1_T - not the one listed in Table 9 but another one in which the double bond was formed at the position with the second largest TA. This conformer will be referred to as Cyen $1_T'$. A comparison of the TAs of caprinolactam hemihydrochloride and those of cycloundec-1-ene $1_T'$ is given in Table 12. The numbering system refers to that used for the lactam and is indicated below.



Further evidence for the existence of the [12323] conformer of cycloundecane has been proposed by Dale[62]. It had been noted[63] that both cis and trans cycloundecene epoxide give

TABLE 12 : Observed TAs (°) for Caprinolactam Hemihydrochloride[58] and calculated TAs (°) for Cycloundec-1-ene $1_T'$.

TA	LACTAM	CYEN $1_T'$
$C_{10}NC_1C_2$	-174	-133
$NC_1C_2C_3$	118	108
$C_1C_2C_3C_4$	-89	-116
$C_2C_3C_4C_5$	52	63
$C_3C_4C_5C_6$	61	89
$C_4C_5C_6C_7$	-176	-172
$C_5C_6C_7C_8$	68	51
$C_6C_7C_8C_9$	65	54
$C_7C_8C_9C_{10}$	-126	-152
$C_8C_9C_{10}N$	54	73
$C_9C_{10}NC_1$	75	74

mixtures of transannular diols by solvolysis and it is suggested by Dale that the [12323] conformer would best allow such hydride shifts to occur. The "bend" produced by a two-bond side here and in other medium rings does not occur in known conformations of larger rings and it may be significant that the 11-membered ring is the largest ring showing such anomalous transannular reactions. Epoxides of larger rings produce only normal 1,2 diols. The "proximity"[23] effect leading to 1,3; 1,4; 1,5 or 1,6 hydride shifts on the opening of 1,2-epoxide rings under acidic conditions is a phenomenon peculiar to medium ring systems.

2.5 PYRROLIZIDINE ALKALOIDS (PAs)

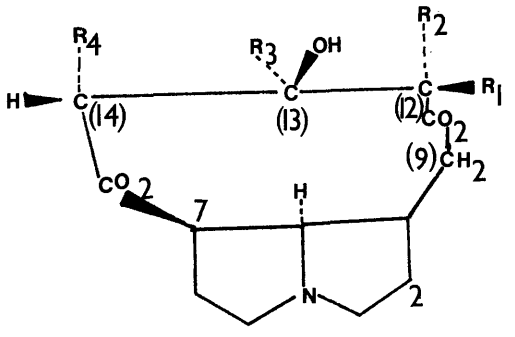
The pyrrolizidine alkaloids[64] constitute a large family based on the pyrrolizidine nucleus. They occur in three main botanical families: Compositae, Borginaceae and Leguminosae. These plant species are spread over the globe and alkaloids have been isolated from them in the western U.S., Canada, New Zealand, Norway and South Africa. Plants of these species e.g. fireweed and poisonous ragwort, have been notorious for over a century for causing cattle diseases. The alkaloids specifically attack the liver, causing tumours.

Chemically, the alkaloids are esters of aminoalcohols (called necines) and carboxylic acids (necic acids). They may be grouped into three classes: simple monoesters, diesters with two monocarboxylic acids and cyclic diesters with a dicarboxylic acid.

Several crystal analyses[65-68] of 11-membered ring PAs have been reported in the literature. They are all cyclic diesters of retronecine possessing a common skeleton which is given in Figure 2.34. The side groups determine the PA concerned.

Fig. 2.34

ALKALOID	R_1	R_2	R_3	R_4
Fulvine[65] (F)	H	CH_3	CH_3	CH_3
Axillarane[66] (A)	OH	$CH(OH)CH_3$	H	$CH_3(CH_3)_2$
Monocratoline[67] (M)	OH	CH_3	CH_3	CH_3
Junceine[68] (J)	OH	CH_2OH	CH_3	$CH(CH_3)_2$



It would seem likely that the 11-membered ring in the PAs should bear a resemblance to some of the calculated cycloundecanes and cycloundecenes - except for that section of the PA ring built from the pyrrolizidine. This is found to be the case: all the alkaloids mentioned in Figure 2.34 have similar conformational features to that of cycloundecane 8 - as shown in Table 13. Cycloundecane 8 can be converted into a cycloundecene (labelled X in Table 13) which shows improved correlation to the alkaloids. This X conformation is also reported in Chapter 5 where it is seen to compare favourably with an observed cycloundecene conformation.

TABLE 13

Ring Torsion Angles for (°):

CYAN 8	X	M[64], F[62a]	A[63b]	J[65b]
-160	-171	-156	-104	-105
148	136	173	-174	-179
-89	-100	-85	125	-122
67	86	52	54	58
-92	-68	-73	-75	-87
167	125	153	111	112
-123	-177	-176	-177	-170
83	114	115	153	163
-122	-90	-27	-19	-24
63	48	-61	-65	-65
58	60	113	94	100

a : Fulvine TAs are reported to be the same as those observed in Monocratoline.

b : Differences in TAs w.r.t. M and F are said to result from crystal packing effects.

2.6 SUMMARY

The preceding sections have introduced some aspects of medium ring conformational analysis with specific emphasis on 11-membered rings.

Cycloundecane is predicted to have a number of low-energy conformations related by small energy barriers of interconversion. The GMEC and the next lowest energy conformation have been observed by x-ray analyses of two previously reported cycloundecane derivatives and are correlated to low energy conformations of cyclononane, cyclodecane and cyclododecane rings.

The predicted GMEC for cycloundec-1-ene is derived from cycloundecane 5 and corresponds to some cycloundecene structures which have been analysed by x-ray diffraction methods and which are introduced in Chapters 5 and 6. X-ray structural analyses on some pyrrolizidine alkaloids produce results which also show conformational resemblance to calculated cycloundecane structures. The correlation between observed and calculated structures is extended to cover an 11-membered ring lactam.

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PART II.

X-RAY DIFFRACTION.

CHAPTER THREE

FUNDAMENTAL PRINCIPLES OF X-RAY DIFFRACTION BY CRYSTALS

3.0 INTRODUCTION

In 1895 Rontgen discovered that when high speed electrons were suddenly stopped by matter, a penetrating radiation was emitted. The nature of this radiation was a subject of argument for several years. In 1912, however, Friedrich, Knipping and Laue showed that the radiation - termed x-rays - had wave properties since they were diffracted by crystals of copper sulphate[1,2].

At first the interest in these experiments lay in the light which they threw on the nature of x-rays, but it soon became clear that they were of even greater importance in providing a means not only of establishing the regularity of atomic arrangement in a crystal, but also of determining exactly what that arrangement was. For from this time onwards, matter of molecular dimensions could be probed by studying the way it scattered x-rays.

The technique of x-ray diffraction was immediately taken up by W.H. and W.L.Bragg[3-7] who improved on the Laue experiment, chiefly by substituting monochromatic for polychromatic x-radiation but also by simplifying the theory of the scattering experiment. In the method initiated by W.L.Bragg, monochromatic x-rays are assumed to be "reflected" from families of regularly spaced planes throughout the crystal. This results in the famous Bragg equation or law. This states that if a diffracted beam is produced when a beam of x-rays passes through a crystal, it must be in such a direction that it may be considered as derived by reflection of the incident beam from one of the sets of lattice planes, but such a "reflection" can only occur if the condition $n\lambda = 2d \sin\theta$ (1) is satisfied. θ is the glancing angle of incidence of the x-ray beam on the plane in question, d is the spacing of the planes in the crystal, λ is the wavelength of the incident x-rays and n is the order of the spectrum. This condition provides a very simple picture of the process of diffraction at a crystal lattice.

X-rays cannot be focussed in the convenient ways used by visible light thus we cannot get a direct image of the atomic pattern in a crystal. Instead, one has to study the diffraction effects produced when x-rays pass through a crystal and build up an image of the structure by calculation. The diffraction of x-rays by crystals is essentially no different from that of visible light by a diffraction grating: but to synthesize the image from the diffracted waves we must use, not lenses, but equations. From the intensities of the reflections collected from a single crystal either photographically or from an automatic diffractometer, it is possible to obtain an electron density distribution in the crystal which, in turn, provides direct images of the atoms in the unit cell.

3.1 FACTORS AFFECTING THE DIFFRACTION INTENSITIES.

The intensity of any reflection is controlled by several factors - the diffracting powers of the atoms, the arrangement of the atoms with regard to the crystal planes, the Bragg angle at which reflection occurs, the number of crystallographically equivalent sets of planes contributing towards the total intensity of each arc or spot and the amplitude of the thermal vibrations of the atoms. Observation of any powder photograph reveals two striking features; firstly, there is general diminution of intensities with increasing reflection angle, and secondly, the intensities vary from one arc to the next in an apparently irregular manner. The general diminution of intensities with increasing reflection angle is due to a decrease in the diffracting power of atoms with increasing angle , to the polarisation of the x-rays on reflection, to a geometrical factor and to the thermal vibrations of the atoms. The apparently irregular variation of intensity from one arc to the next is due to the effect of the relative positions of the atoms in space - the structure factor - and to the variation in the number of equivalent sets of planes contributing to the spot or arc - a number which depends on the type of plane. It is the structure factor in which we are chiefly interested but in order to isolate it we must allow for all the other factors. These factors can be classified into those having a geometrical basis and certain others having a physical basis. They are discussed more fully below.

(a) Geometrical factors affecting intensities.

Atoms in crystals cannot be regarded as scattering points: the "diameter" of the electron cloud of an atom is of the same order of size as the distance between the centres of adjacent atoms. The consequence of this is that there can be destructive interference between the wavelets scattered by the electrons in an atom which reduces the intensity of the resultant diffracted beam. The reduction of intensity is not considerable for

reflections from widely spaced planes. However, for the higher order diffractions, when the phase difference for waves from the inner regions of adjacent atoms is several wavelengths, waves from regions of not very dissimilar electron densities interfere with each other, and the intensity of the resultant diffracted beam is, therefore, much reduced. This would appear to introduce considerable complexity into the problem of calculating the intensities of diffracted beams. Fortunately, it can be dealt with in quite a simple way, i.e. by treating an atom as if it had all its diffracting matter at a point (the centre of the atom) , but with a diffracting power diminishing with the spacing of the reflecting planes. The effective diffracting power of each atom is usually given as a function of $(\sin\theta) / \lambda$ and the diffracting powers of all atoms (symbolised f) for a wide range of $(\sin\theta) / \lambda$ are available both in the original literature[8-12] and in the International Tables for X-ray Crystallography[13].

As mentioned previously, another cause of diminution of the intensities of x-rays with increasing angle of reflection is the polarisation which occurs on reflection. Non-polarised radiation is ordinarily used in x-ray crystallography, however, it is found that the emergent radiation is partially polarised. This results from those electric vectors which are parallel to the surface of the reflecting plane being reflected more efficiently than those which are perpendicular to this plane. The intensity of the reflected beam is corrected by the polarisation factor, p, which depends only on the angle θ and which is unaffected by the x-ray method employed: p is given by

$$p = 1/2 \ (1 + \cos^2 2\theta) \quad (2)$$

Another angle factor affecting the intensity of the reflection is known as the Lorentz factor, L, which expresses the relative time any crystal spends within the narrow angular range over which reflection occurs. In terms of the concept of the reciprocal lattice, each point h,k,l of that lattice has a finite

size, and as the reciprocal lattice rotates through the sphere of reflection, each point spends a finite time passing through the surface of this sphere. This factor varies with the distance of the reciprocal lattice point from the origin which is, of course, related to the angle of reflection. The Lorentz factor also depends on the technique employed to measure the intensities. For data collected on a four circle diffractometer, L is given by:

$$L = 1 / \sin 2\theta \quad (3)$$

The combined Lorentz polarisation (Lp) factor for a four circle diffractometer may then be written as:

$$Lp = (1 + \cos^2 2\theta) / 2\sin 2\theta \quad (4)$$

(b) Some physical factors affecting intensities.

These factors arise in a less simple fashion and are due to absorption and the thermal motion of the atoms.

Absorption of x-rays by a crystal may reduce the diffracted intensity by a large factor. Even when the crystal is not large enough to give complete absorption of the incident beam, absorption may reduce the intensity of the diffracted beam by a considerable amount. It is not possible to give a general treatment of the intensity reduction. In structure determination, it is often simplest to choose a crystal small enough and a radiation penetrating enough and ignore the variation of absorption with crystal orientation. The effects of absorption can only be ignored for rough work. The amount of absorption which takes place during the transmission of x-rays through the crystal while a particular reflection is being produced is very tedious to calculate, since it is a function of the shape of the crystal and the relationship of the direct and diffracted beams to this shape. While it is ordinarily out of the question to spend the time making an exact allowance for

absorption it is often possible to approximate the allowance. Such an approximation leads to a coefficient termed the linear-absorption coefficient which applies to the absorption of a particular monochromatic radiation by a particular material. The linear-absorption coefficient for any crystal can be computed from a knowledge of its chemical compostion, its density and a table of mass absorption coefficients of the elements. Such a table is given in Vol.III of International Tables for X-ray Crystallography[13]. The mass-absorption coefficients are functions not only of the elements but also of the wavelength of the x-radiation employed.

In discussing the intensity of the x-ray diffraction spectra it has been assumed that the crystal structure is a static one i.e. that it can be thought of as a periodic pattern of stationary atoms. Temperature modifies this situation since it causes every atom to undergo thermal motion. The general nature of the modification can be appreciated by noting that the effect of the thermal motion is to make the electrons of each atom sweep out a larger average volume than they would occupy if the atom were at rest. The effective scattering factor for an atom in thermal motion is less than that for an atom at rest and the amount of the reduction depends on its mean-square displacement in the direction bisecting the angle between the direct and the scattered beam. For an atom in a crystal reflecting at a Bragg angle this will be the direction perpendicular to the reflecting planes. In principle, the mean-square displacement could be calculated in terms of the temperature of the crystal and the interatomic forces , but in practice, one is more likely to obtain information about interatomic forces from the effect of temperature on x-ray diffraction than vice-versa. Waller[14] showed that a fair approximation to the effect of thermal motion on the intensity of x-ray reflection can be made for isometric structures containing only one kind of atom. In this simple case,

$$f_j = f_0 \exp[-B(\sin^2\theta) / \lambda^2] \quad (5)$$

where f_0 is the scattering power of the stationary atom and f_j is the scattering factor for isotropic vibration. $B = 8\pi^2U^2$, the Debye-Waller factor or the isotropic thermal parameter. It usually lies in the range 2-4 Å for carbon and oxygen atoms in a typical organic crystal and it is temperature dependent. U^2 = the mean square amplitude of vibration perpendicular to the reflecting plane and lies in the range 0.1-0.01 Å^2. It is a very complex matter to make an allowance for thermal motion. Each atom undergoes a motion such that its electron density is smeared over a small anisotropic volume, usually regarded as a triaxial ellipsoid. Each non-equivalent atom not only has a different ellipsoid, but the ellipsoids are oriented differently. To describe such an ellipsoid, six parameters are needed - three give the radii along its principal axes and three more describe the orientation of the ellipsoid in space. Thus, for anisotropic vibration,

$$f_j = f_0 \exp[-(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{13}hla^*c^* + 2B_{23}klb^*c^* + 2B_{12}hka^*b^*)/4] \quad (6)$$

where B_{ij} is the anisotropic thermal parameter and a^*, b^*, c^* are the lengths of reciprocal cell edges.

Alternatively, equation (6) may be rewritten in the more commonly used form:

$$f_j = f_0 \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{13}hla^*c^* + 2U_{23}klb^*c^* + 2U_{12}hka^*b^*)] \quad (7)$$

where $U_{ij} = U_{ij}^2 = B_{ij} / 8\pi^2$, the thermal parameters expressed in terms of mean square amplitudes of vibrations.

3.2 THE STRUCTURE FACTOR.

The wave scattered by a crystal can be characterised by a quantity F_{hkl}. This is a complex quantity whose magnitude is the amplitude of the scattered wave and whose direction in the complex plane is determined by the phase of the scattered wave. Since this factor depends on the arrangement of matter in the specific crystal under discussion i.e. on its crystal structure, the factor is commonly called the structure factor (SF). The SF equation can be written in the form:

$$F(hkl) = \Sigma_{j=1}^{n} \; f_j \exp 2\pi i(hx_j + ky_j + lz_j) \quad (8)$$

where f_j is the aforementioned scattering factor and $2\pi(hx_j + ky_j + lz_j)$ is the phase angle, ϕ_j, expressed as a function of the fractional coordinates x_j, y_j, z_j of the J atoms of the unit cell.

For purposes of computing SFs it is usually convenient to express them in terms of their real and imaginary components :

$$F(hkl) = A(hkl) + iB(hkl) \quad (9)$$

where i is the imaginary number $(-1)^{1/2}$ and

$$A(hkl) = \Sigma_{j=1}^{n} \; f_j \cos 2\pi(hx_j + ky_j + lz_j)$$

and

$$B(hkl) = \Sigma_{j=1}^{n} \; f_j \sin 2\pi(hx_j + ky_j + lz_j).$$

From the SF equation it follows that the magnitude of the SF i.e. the SF amplitude, may be given by

$$|F(hkl)| = \{A(hkl)^2 + B(hkl)^2\}^{1/2} \quad (10)$$

The intensity of each diffracted beam I(hkl) is normally proportional to the square of the modulus of the structure amplitude,

$$I(hkl) \propto |F(hkl)|^2 \quad (11)$$

The phase angle of F(hkl) can also be deduced from the SF equation:

$$\tan \phi_{hkl} = B(hkl) / A(hkl) \quad (12)$$

3.3 STRUCTURE FACTORS AND THE ELECTRON DENSITY DISTRIBUTION.

It is well known that a periodic function can be represented by an appropriate sum of cosine and sine terms known as a Fourier series. Since a crystal is periodic, its electron density can be neatly represented by such a series:

$$\rho(xyz) = V^{-1}\Sigma_h\Sigma_k\Sigma_l\ F(hkl)\ \exp[-2\pi i(hx + ky + lz)] \quad (13)$$

where $\rho(xyz)$ is the electron density at the point with fractional coordinates x,y,z in the unit cell of volume V. The triple summation is taken over all diffracted beams.

It can be shown that

$$F(hkl) = |F(hkl)|\ \exp[2\pi i\phi_{hkl}] \quad (14)$$

Using equation (14) and substituting for F(hkl) in equation (13) results in a more useful form of the Fourier expression:

$$\rho(xyz) = V^{-1}\Sigma_h\Sigma_k\Sigma_l\ |F(hkl)|\exp[-2\pi i(hx + ky + lz - \phi_{hkl})] \quad (15)$$

The final electron density represents the distribution of atoms in the unit cell of a crystal. Thus the utilisation of the electron densities and the reasons for their calculation are self-evident. In practice, however, it is not a simple matter to carry out the summations. This is because the coefficients necessary for the series summation are incompletely known. Only the SF magnitudes are determined experimentally while the phase relations must be derived by some other strategy e.g. trial and error, the heavy atom method, isomorphous replacement, Patterson methods or Direct methods. This search for a self-consistent set of phases is termed the "phase problem" of crystallography.

3.4 DIRECT METHODS OF PHASE DETERMINATION.

The earliest method for solving crystal structures was a process of trial and error. Possible structures were postulated and the calculated and observed intensities compared in order to test the plausibility of the postulates. The advent of the Patterson function method marked an important advance: an examination of the vector map coupled, perhaps, with chemical knowledge may yield important information containing the orientation or relative position of groups of atoms, or even enable a complete structure determination to be made. When the structure is centrosymmetric and contains a few atoms of high atomic number then the position of these "heavy" atoms may sometimes be found unequivocally by an examination of the Patterson function. A Fourier synthesis, calculated with the observed structure amplitudes and with phases (0 or pi) given by the combinations of the heavy atoms, will then often show the electron density associated with the remaining atoms of the structure. In such a case the structure may be considered to have been determined directly, in the sense that a series of operations led from the diffraction data to the structure. There are various other procedures more or less related to the Patterson function, such as the use of the Patterson-Harker[15] function or the examination of a weighted reciprocal lattice[16], which, under suitable conditions, may also give a direct determination of a crystal structure.

The adjective "direct" however, is usually reserved for those methods which attempt to derive the phases of the SFs directly by mathematical means from the x-ray diffraction data. Direct methods are usually cast in the form of a mathematical problem which, once formulated, may be solved by a sequence of steps in which any decisions are of a purely mathematical nature.

In the heavy atom,method once the heavy atom or atoms are correctly located in the unit cell the relative phases of the SFs can be determined unambiguously. These relationships

between relative SF magnitudes and their phases has focussed attention on the fact that the observed intensities do contain information regarding phases, even though it is not directly apparent. Direct methods seek to determine phase information objectively by examination and comparison of SF magnitudes derived from the study of a single crystal. Starting from the fundamental physical fact that there can be no regions of negative electron density within the unit cell, it is possible to derive a number of inequalities, equalities and probabilities which, in favourable cases, allow phases to be determined.

(a) Inequality relationships.

The hereditary origin of all direct methods may be traced back to the inequality relationships between SFs first expounded by Harker and Kasper[17]. These expressions, resulting from the combination of SF expressions with certain classical inequalities, provided the first means of determining the phase of one reflection in terms of its magnitude and those of others.

(b) Equalities.

The next impetus to the development of direct methods was initiated by Sayre[18] who showed that for a structure containing equal resolved atoms, the SFs are interrelated by precise equations. It can be shown that for three reflections represented as $\underline{h}$, $\underline{k}$, $\underline{h}-\underline{k}$:

$$F\underline{h} = \phi\underline{h} \sum_{\underline{k}} F\underline{k} \cdot F\underline{h}-\underline{k} \quad (16)$$

where ϕ_h is simply a calculable scaling term. When the sum of the products on the right of (16) is examined, it is clear that, for a very large product i.e. when a particular $F\underline{k}$ and $F\underline{h}-\underline{k}$ are both large, this product dominates the sum, and hence the sign, of $F\underline{h}$. Expressing the sign of $F\underline{h}$ by $S\underline{h}$, relation (16) means

that

$$S\underline{h} = S\underline{k} \cdot S\underline{h}-\underline{k} \quad (17)$$

This relationship is termed a "Sigma two" relationship and may also be applied to non-centrosymmetric cases in which S is used to denote "the phase" . This equation indicates that a knowledge of the signs of two reflections permits the sign of the third reflection to be determined. The restricting condition is that the structure concerned must be composed of identical atoms. For organic crystals equation (17) has been shown to hold if the associated SFs are large - excepting hydrogen, the predominant components of organic crystals are carbon, oxygen and nitrogen which have roughly equivalent atomic weights which deems them to be composed of "equal" atoms.

(c) Probabilities.

Both Sayre's equation and Harker-Kasper inequalities require that the SFs should be large and they both suggest that the sign relationship is probably more true than not, even if the SFs are not quite large enough to make the relationship a certainty. In the uncertain situation the "equals" sign in equation (17) should be replaced by "probably equals".

The question of the exact probabilities of equation (17) is obviously an important one and the result given by Cochran and Woolfson[19] is most commonly used as it is sufficiently accurate for most purposes while not being too mathematically intricate. This result is that the probability of the sign relationship holding is given by

$$P = 1/2 + 1/2 \tanh(|E\underline{h}.E\underline{k}.E\underline{h}-\underline{k}|N^{-1/2}) \quad (18)$$

i.e. in terms of normalised SFs termed E values.

By regarding each phase indication as a vector of length $|E\underline{k}.E\underline{h}-\underline{k}|$ and direction $[\phi\underline{k} + \phi\underline{h}-\underline{k}]$, they may be summed vectorially. This operation leads to the Tangent formula:

$$\tan \underline{h} = \{\Sigma_k |Ek.Eh-k| \sin[\phi k + \phi h-k]\} / \{\Sigma_k |Ek.Eh-k| \cos[\phi k + \phi h-k]\} \quad (19)$$

Refinement of a set of phases can be achieved by a recycling process, employing the Tangent formula, which can be continued until negligible shifts in the derived phase angles are observed from one cycle to the next.

Both the equality and probability relationships mentioned here have dealt with three-phase structure invariants termed triplets. The probability of the sign of a triple phase invariant holding, depends on the size of the E-magnitudes involved in the construction of the invariant. It is, therefore, reasonable to assume that the invariant will be more sensitive to some E-magnitudes than others. In an attempt to define the criteria which bring about this dependence on E-magnitudes, the concept of "nested neighbourhoods" was introduced[20]. This has produced additional probability formulae which deal with four-phase structure invariants termed quartets, and with five-phase structure invariants termed quintets. Major changes may result as one increases the number of magnitudes on which the estimate for the structure invariant depends. The two simplest formulae[21,22] for estimating the sign of a quartet of reflections and its associated probability are the 7-magnitude two neighbourhood $P_7\pm$ formula and the 13-magnitude three neighbourhood $P_{13}\pm$ formula.

3.5 PHASE DETERMINATION IN PRACTICE.

A number of methods have been used to apply equation (17) and its derivatives to the problem of practical phase determination and various computer programmes have resulted from these methods. The MULTAN[23] system is a package of crystallographic computer programmes which employs the "symbolic addition method" of the Karles[24] to determine phases and is the system used by the author.

The principle of the symbolic addition method is that one starts with a limited number of phases and uses these to pyramid to a number large enough to give a reasonable Fourier representation of the structure. The initial problem is to obtain a set of starting reflections which will efficiently expand to give new phase information. This is the most difficult part of any multi-solution technique. Once the normalised SFs have been calculated a subset is chosen for carrying out sign determination. In the case of centrosymmetric crystals the sigma-2 relationship is used for sign determination (equation (17)). The procedure is similar for non-centrosymmetric structures.

In order to define a crystal structure completely it is necessary to set up a system of axes with a fixed origin. A change in origin position will affect the phases but not the magnitudes of the SFs, so the selection of a particular origin imposes a corresponding pattern of relative phases on the diffraction pattern. It is possible to put reflections into categories according to whether or not their signs depend upon origin position in the x, y or z direction - termed the parity of h, k or l. Although the signs of the individual phases depend on the structure and choice of origin, there exists certain linear combinations of phases, the structure invariants, whose values are independent of origin choice. The occurrence of structure invariants lends itself to the rule that reflections used to define the origin cannot combine to give a structure

invariant and are, therefore, linearly independent. Parity arguments further restrict the choice of reflections used for origin definition. The origin defining reflections form a good starting point for phase determination.

The MULTAN system is composed of the following main subprogrammes:

(i) NORMAL: computation of normalised structure amplitudes.

(ii) MULTAN: this procedure is composed of five logical parts, two of which are optional and will not be discussed further. Sigma-2 finds sets of sigma-2 relationships. It also serves to load quartets into the system and collate them with the sigma-2s if required. Converge uses the supplied space group information to determine which parity groups are required to define the origin: it then calculates the probabilities for the signs of the structure invariants via the Tangent formula[19]. Fastan determines the phases of other high value E-magnitudes by using the starting set determined by Converge. It employs a weighted version of the Tangent formula and the phase relationships output by the sigma-2s. A figure of merit based on the degree of internal consistency is given to each complete phase set.

(iii) FOURIER: this procedure contains the remaining programmes in the MULTAN system, EXFFT and SEARCH, which normally run consecutively to calculate and interpret E-maps. EXFFT produces the E-map from a set of normalised SFs which has the highest combined figure of merit. SEARCH looks for the largest peaks in the E-map and lists their coordinates in order of peak height.

For each set of phases determined, three figures of merit (FOM) are computed and output with the Tangent formula results. If quartets are available, a further FOM is introduced. The "absolute" FOM is a measure of internal consistency among the sigma-2 relationships - it is zero for random phases and close to

unity for the correct set of phases. The next FOM, PSI(zero), is a powerful discriminator against incorrect sets of phases as it is very sensitive to molecular position and is independent of the Tangent formula - it is expected to be small for a good set of phases. Finally the third FOM, RESID, is a measure of the extent to which the "squared structure" resembles the "structure" for the set of phases under consideration - it should be a minimum for the correct set of phases. After all sets of phases have been computed, MULTAN outputs a summary of the FOMs including a combined FOM, which has been found to be a more reliable indicator of the correct set of phases than any of the other FOMs separately and it is used by EXFFT to decide on the order of computation of E-maps - it has a maximum value for the best set of phases.

MULTAN has greatest success when dealing with centrosymmetric crystals of small organic molecules whereas non-centrosymmetric crystals introduce further complications. However, complete structural solutions have been obtained for both sets of crystals via MULTAN.

3.6 FOURIER SYNTHESIS

Once a set of phases has been determined, it is possible to calculate the electron density by using equation (15) and the observed SF amplitudes. If the structure model used to calculate the phases is entirely correct, the electron density calculation should produce the proposed atomic coordinates exactly. It is evident that the general departure of the computed from the observed intensities must increase with the departure of the model from the actual structure. A common measure of the extent to which refinement of the atomic positions has progressed is the so-called residual index, R, defined by

$$R = \Sigma \{ |Fo| - |Fc| \} / \Sigma |Fo| \quad (20)$$

where $|Fo|$ is the modulus of the observed value of the SF and $|Fc|$ is the modulus of its calculated value. The value of R that can be considered satisfactory depends to some extent on the accuracy of the intensity measurements and on the complexity of the structure, but typically one would aim at values of less than 8% for counter measurements.

The most obvious method of refinement is simply successive cycles of Fourier synthesis. The first Fourier synthesis, based on heavy atom positions or sign relationships, will probably yield approximate positions for lighter atoms, which were not used for the derivation of the initial sets of phases, or will yield corrected coordinates for the previous set of atoms. The phases of the SFs can then be recalculated using this additional information. This process of repeating the synthesis with phases calculated for the atomic positions given by the preceding synthesis can be repeated until no significant change in atomic positions is found on repetition. The value of R can be calculated at each stage and the extent to which it decreases is an indication of the rate at which the refinement is proceeding.

When the analysis has reached the stage where phases can be

assigned to all observed reflections it by no means follows that the electron density peaks indicate the best coordinates. There are still termination-of-series errors present. Difference synthesis is one device for correcting these errors: the Fourier series refinement is continued but instead of using |Fo| for the amplitudes, the algebraic difference (Fo-Fc) is substituted in equation (13). The resulting difference Fourier map is particularly useful for the most precise location of atomic positions, for the identification of missing atoms and for refinement of thermal parameters.

3.7 LEAST SQUARES REFINEMENT.

Another device for dealing with termination-of-series errors is the least squares refinement. As there is a large excess of observational data (Fo) over structural parameters (atomic coordinates, in the first instance), there is the typical situation where the least squares method can be applied. The computation can be set up so as to indicate the small shifts in coordinates which will minimise the sum, $\Sigma(Fo-Fc)^2$, or some related quantity, for all the observed reflections. If desired, weights may be introduced into this equation, to allow for variations in the accuracy with which the measurements of the different reflections have been made. The function most commonly used is

$$R = \Sigma_{hkl}\, w_{hkl}(\,|Fo| - |Fc|\,)^2 \quad (21)$$

where the sum is over the set of crystallographically independent observed planes and w_{hkl} is a weight for each term. If the standard deviation for each $|F(hkl)|$ is $\sigma(hkl)$, the value of w which gives the lowest standard deviations in the derived parameters may be shown to be

$$w(hkl) = 1 \,/\, \sigma^2(hkl) \quad (22)$$

Let p_1, p_2 ..... p_n be n parameters occurring in the $|Fc|$ whose values are to be determined. For R to be a minimum we must have

$$\delta R \,/\, \delta p_j = 0 \quad (j = 1.....n) \quad (23)$$

$$\text{i.e. } \Sigma_{hkl}\, w\, D\, \delta|Fc| \,/\, \delta p_j = 0 \quad (24)$$

where $D = |Fo| - |Fc|$. The parameters have to be varied until these n conditions are satisfied. For a trial set of p_j close to the correct values we may expand D as a function of the parameters by a Taylor series to the first order

$$\Delta(p + \varepsilon) = \Delta(p) - \Sigma_{i=1}^{n} \varepsilon_i \left(\delta Fc / \delta p_i \right) \quad (25)$$

where ε_i is a small change in a parameter p_i and p and ε stand for the whole set of parameters and changes, and the minus sign appears before the summation since D = |Fo| - |Fc| and it is the changes in |Fc| which are to be considered.

Substituting (25) in (24) and expressing the result in matrix notation since there are n of these equations for j = 1....n needed to determine the n unknowns, produces the Normal equations:

$$\Sigma_i \, a_{ij} \, \varepsilon_{ij} = b_j \quad (26)$$

where

$$a_{ij} = \Sigma_{hkl} \, w \, \{ \delta Fc / \delta p_i \} \{ \delta Fc / \delta p_j \} \quad (27)$$

$$b_j = \Sigma_{hkl} \, w \Delta \{ \delta Fc / \delta p_j \} \quad (28)$$

It is the Normal equations which must be set up and solved to refine a structure.

Regardless of the exact function used, the approximations employed in constructing the least squares equations limit this application to the refinement of reasonably accurate initial parameters. It is not possible to solve for the parameters directly from the intensity data by this method, without first developing the structure by one of the methods described earlier. It is also possible to include a temperature factor and a scale factor in the least squares procedure. In its simplest form, each atom is assumed to have the same isotropic temperature correction. A somewhat more elaborate device is to include an isotropic temperature factor which is different for each atom. Finally, the thermal motion of each atom can be assumed to be not only different but anisotropic. This would give three positional parameters and six temperature factors for each atom.

Some better method for the assessment of accuracy is desirable and it has now become established practice, in all

precise analyses, to state estimated standard deviations for the atomic coordinates and for the derived molecular dimensions.

3.8 SUMMARY.

This chapter has dealt with the basic theory of x-ray diffraction by crystals. There follows a summarised outline of crystal structure analysis.

1. Selection and preparation of a crystal for which intensity data is collected.

2. Conversion of intensities to amplitudes with allowance for several geometrical and physical factors.

3. Direct solution of the crystal structure.

4. Refinement of the crystal structure.

5. Calculation of structural data (interatomic distances and angles).

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CHAPTER FOUR

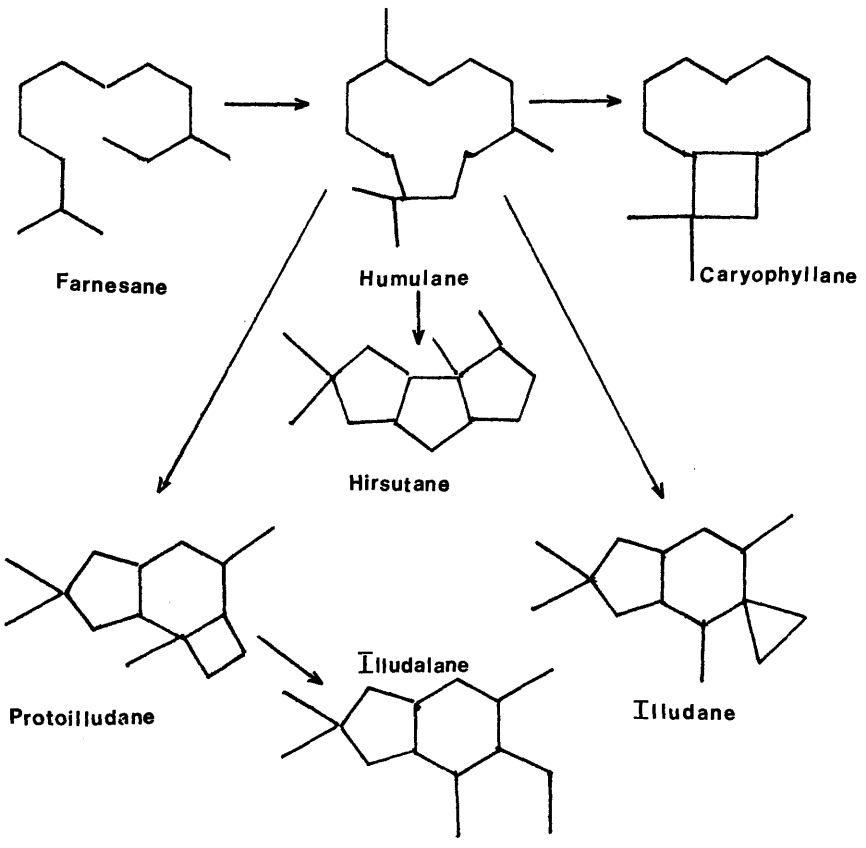
AN X-RAY ANALYSIS OF THE 2,4 DINITROPHENYLHYDRAZONE DERIVATIVE OF THE SESQUITERPENOID, ZERUMBONE.

4.0 FOREWORD.

Sesquiterpenoids are usually characterised as compounds having a basic skeleton of fifteen carbon atoms formed, similarly to other terpenoids, by a regular repetition of the basic isoprene unit, and occurring mainly in plant material. In recent years, sesquiterpenoids have been encountered in the animal kingdom and the number of exceptions to the isoprene rule increases daily, suggesting that the basic definition has to be widened. Parallel with the broad occurrence of sesquiterpenes, there is a rich variety of structures among these sesquiterpenes. They have also been classified according to their biogenetical relations.

Figure 4.1 introduces a group of types which belong to an interesting group of sesquiterpenoid derivatives from higher fungi: they are termed as the Humulane class of sesquiterpenoids and their biogenetic relationships are also indicated.

FIG. 4.1

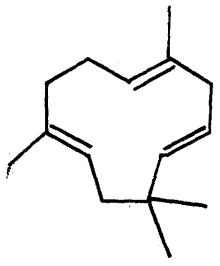


The simpler terpenoids have been known for many centuries as plant constituents whose fragrance commended them to the early investigators. The subsequent discovery of terpenoids in animal sources and the recognition of the structural similarities between terpenoids and steroids has suggested a common biogenetic origin of these two classes of compounds. Systematic study of the properties and the reactions of natural and synthetic terpenoids and steroids has helped to reveal the intricate relationships of structure, stereochemistry, reactivity and mechanism and it is here, perhaps, that they have proved of greatest value to the chemist. For, with their structural rigidity and variety of substitution, these molecules are ideal model compounds: in this role they have been used with conspicuous success for the development of new synthetic reactions, for the correlation of molecular structure with physical properties and for testing theories of reaction mechanisms.

The x-ray analysis of the 2,4-dinitrophenylhydrazone derivative of zerumbone has been undertaken to provide conformational information both to assist comparison with the stereochemistry of humulene derivatives and as part of a study of eleven-membered ring compounds.

4.1 AN INTRODUCTION TO HUMULENE AND ZERUMBONE.

The sesquiterpene hydrocarbon known as humulene and only recently shown to be a mixture[1], was first isolated from hops (Humulus lupulus L) by A.C.Chapman[2]. It is also found in Populus nigra L[3]., in Agonis abnormis[4] and in Lindera strychnifolia[5]. A suggestion by E.Deussen[6] that humulene was identical with α-caryophyllene was supported by Sorm[7] and his colleagues who showed that humulene contained three double bonds and is, therefore, monocyclic. Various experimental investigations[8,9] substantiated this relationship. The basic structure of humulene was confirmed by the synthesis[10] of humulane. Unfortunately much confusion concerning the positions of the double bonds has arisen due to the failure to recognise humulene as a mixture. The predominant sesquiterpene of hop oil has the structure shown in Figure 4.2 and is termed α-humulene. The x-ray analysis of the silver nitrate adduct of α-humulene was undertaken by two groups of workers[11,12] who defined the stereochemistry of α-humulene as that shown in Figure 4.2 i.e. the all trans structure.



α-HUMULENE

Fig. 4.2

Zerumbone is a crystalline sesquiterpenoid ketone of the formula ($C_{15}H_{22}O$) which was first extracted from the roots of the wild ginger plant, Zingiber zerumbet, by N.S.Varier in 1944[13]. It was assigned the structure shown in Figure 4.3 on the basis of various chemical and spectroscopic investigations[14-16].

ZERUMBONE

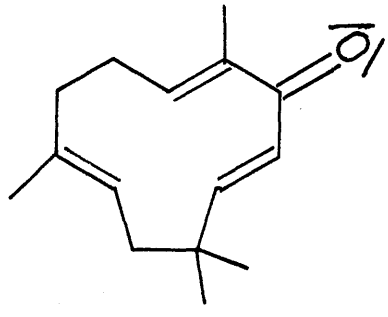


Fig. 4.3

In view of the compound's close similarity to humulene, the double bonds in zerumbone are believed to have trans stereochemistry. It was decided that an x-ray investigation of zerumbone would be undertaken to solve this question. The crystals of zerumbone were unacceptable for x-ray analysis so a derivative was prepared.

4.2 EXPERIMENTAL

The zerumbone was gifted by Professor J.K.Sutherland to whom I extend my thanks. Professor G.A.Sim kindly prepared the 2,4-dinitrophenylhydrazone derivative of zerumbone by a standard procedure[17]. This derivative was used in the x-ray analysis which follows. It was crystallised from ethanol.

Crystal Data.

Zerumbone (2,6,9,9-tetramethylcycloundeca-2,6,10-trienone) 2,4-dinitrophenylhydrazone, $C_{21}H_{26}N_4O_4$, M = 398.50 amu, monoclinic, $\underline{a}$ = 12.619(2), $\underline{b}$ = 7.290(3), $\underline{c}$ = 23.422(3) Å, β = 98.06(1)°, U = 2133.4 Å^3, D$\underline{c}$ = 1.24 g.cm.$^{-3}$, Z = 4, F(000) = 848, μ(Cu-K$_\alpha$) = 7.2 cm.$^{-1}$, Space Group = $P2_1/c$.

Data Collection.

Instrument used: Enraf-Nonius CAD4 diffractometer.
Radiation used : Cu-K$_\alpha$, λ = 1.5418 Å.
Monochromation used: graphite crystal.
Upper limit for data collection: Θ_{max} = 72°.
Number of independent observed reflections: m = 3222.
Unobserved cut-off: $2.5\sigma_I$.
Number of parameters refined: n = 366.
Number of reflections per parameter: m/n = 8.80.

Cell dimensions were derived from least-squares treatment of the setting angles for 25 reflections. For intensity measurements, 4856 reflections $\underline{hkl}$ and $\underline{hk\bar{l}}$ were surveyed in the range $\Theta \leqslant 72°$ and 3222 reflections satisfied the criterion, $I > 2.5\sigma_I$.

Structure Analysis.

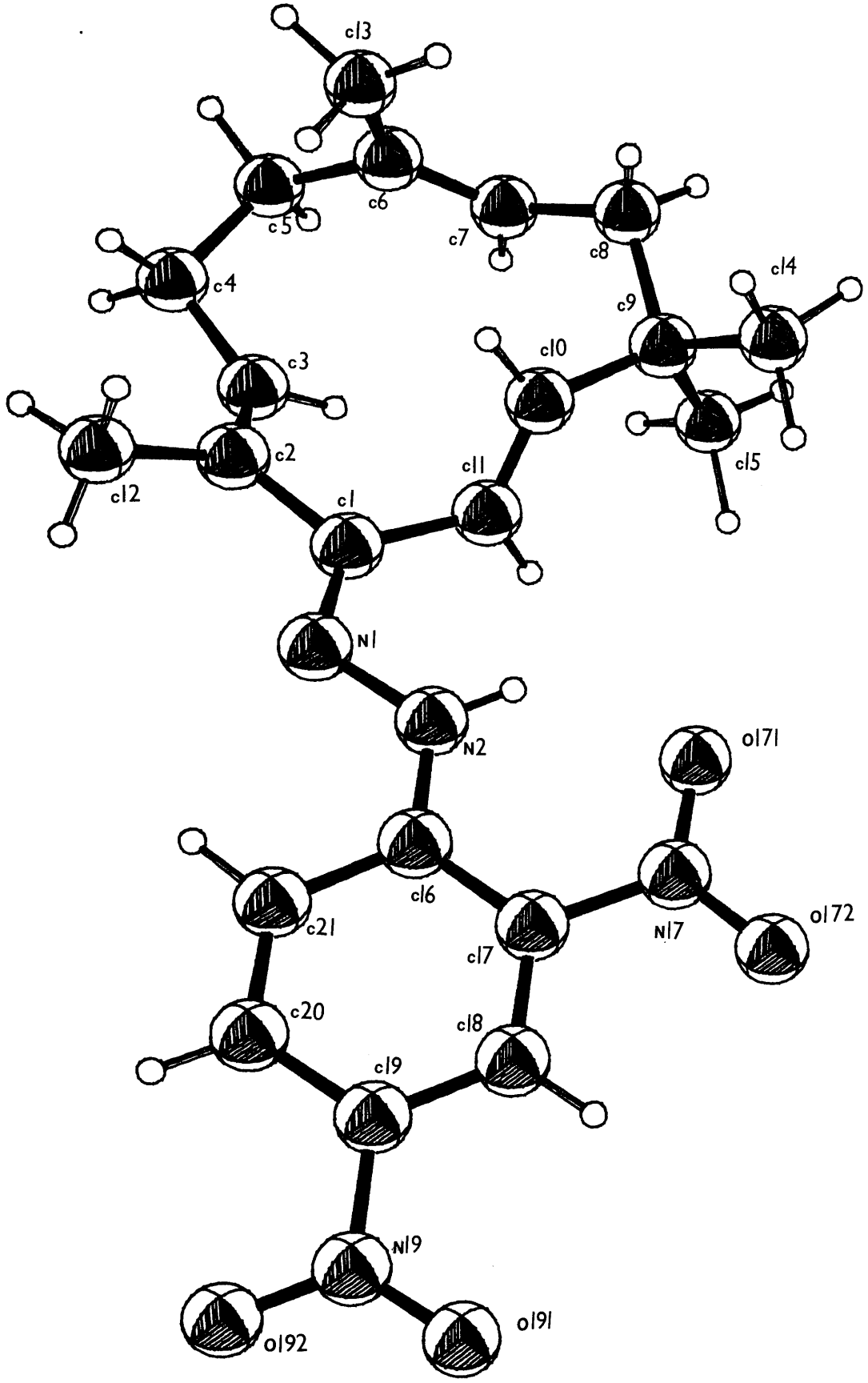
The crystal structure was elucidated by the direct phase-determining program MULTAN[18]. Sixteen phase sets were

calculated for the top 216 |E|s with $E \geqslant 2.00$. An E-map computed from the set with the highest combined figure of merit revealed all the non-hydrogen atoms.

Full-matrix least-squares adjustment of positional and isotropic thermal parameters of the C, N and O atoms converged at R = 0.164. Anisotropic refinement of all non-hydrogen atoms produced an R value of 0.10. The hydrogen atoms were then located in a difference electron-density distribution and included in the least-squares calculations with isotropic thermal parameters. The weighting scheme was changed from unity to $w = 1/\sigma^2(\underline{F})$ and R converged to 0.046, $R_w = 0.052$.

Fourier and least-squares calculations were performed with the SHELX[19] series of programs and the molecular diagram of Figure 4.4 was prepared by ORTEP[20].

FIG. 4.4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O191
O192

4.3 RESULTS

Final structure factors (observed and calculated) are included in the appendices.

TABLE 1: Fractional atomic coordinates (x/a, y/b, z/c) ($x10^4$) with estimated standard deviations (esd's) in parentheses for the non-hydrogen atoms.

TABLE 2: Thermal parameters for non-hydrogen atoms (U_{11}, U_{22}, U_{33}, U_{23}, U_{13}, U_{12}) ($x10^3$ Å^2).

TABLE 3: Fractional atomic coordinates (x/a, y/b, z/c) ($x10^3$) and U isotropic ($x10^3$ Å^2) for hydrogen atoms.

TABLE 4: Interatomic bonded distances (Å).

TABLE 5: Valence angles (°).

TABLE 6: Torsion angles (°).

TABLE 7: Interatomic bonded distances for hydrogen atoms. (Å).

TABLE I

C(1)	11464(1)	0166(2)	-1487(1)
C(2)	11149(1)	-0552(2)	-2078(1)
C(3)	11849(1)	-0426(3)	-2451(1)
C(4)	11814(2)	-1335(4)	-3025(1)
C(5)	12953(2)	-1959(4)	-3109(1)
C(6)	13516(2)	-2919(3)	-2583(1)
C(7)	14292(2)	-2047(4)	-2236(1)
C(8)	14786(2)	-2623(4)	-1642(1)
C(9)	14437(1)	-1401(4)	-1153(1)
C(10)	13234(1)	-1228(3)	-1282(1)
C(11)	12626(1)	0234(3)	-1266(1)
C(12)	10063(2)	-1410(3)	-2218(1)
C(13)	13075(2)	-4744(4)	-2458(1)
C(14)	14984(2)	0467(5)	-1132(1)
C(15)	14734(2)	-2380(6)	-0573(1)
C(16)	10421(1)	1838(2)	-0293(1)
C(17)	10740(1)	2301(2)	0298(1)
C(18)	10049(1)	3149(2)	0620(1)
C(19)	9029(1)	3542(2)	0372(1)
C(20)	8666(1)	3061(2)	-0197(1)
C(21)	9341(1)	2230(2)	-0520(1)
N(1)	10718(1)	0613(2)	-1189(1)
N(2)	11084(1)	1103(2)	-0627(1)
N(17)	11806(1)	1920(2)	0584(1)
N(19)	8334(2)	4549(2)	0708(1)
O(171)	12456(1)	1169(2)	0317(1)
O(172)	12027(1)	2329(3)	1093(1)
O(191)	7476(1)	5083(2)	0457(1)
O(192)	8642(2)	4851(2)	1217(1)

TABLE 2

C(1)	53(1)	56(1)	50(1)	-2(1)	4(1)	-7(1)
C(2)	53(1)	57(1)	48(1)	-3(1)	-1(1)	1(1)
C(3)	59(1)	70(1)	48(1)	0(1)	1(1)	1(1)
C(4)	71(1)	100(2)	45(1)	-3(1)	3(1)	7(1)
C(5)	74(1)	127(2)	54(1)	-10(1)	15(1)	3(1)
C(6)	54(1)	105(2)	68(1)	-13(1)	15(1)	6(1)
C(7)	53(1)	114(2)	71(1)	-4(1)	17(1)	1(1)
C(8)	45(1)	124(2)	85(1)	1(1)	3(1)	4(1)
C(9)	43(1)	116(2)	63(1)	8(1)	-2(1)	-14(1)
C(10)	45(1)	87(1)	48(1)	3(1)	0(1)	-12(1)
C(11)	56(1)	79(1)	51(1)	-11(1)	5(1)	-17(1)
C(12)	55(1)	84(1)	60(1)	-15(1)	0(1)	-6(1)
C(13)	73(1)	100(2)	101(2)	-11(2)	5(1)	4(1)
C(14)	58(1)	136(2)	85(2)	2(2)	-1(1)	-34(1)
C(15)	60(1)	159(3)	79(1)	28(2)	-14(1)	-15(2)
C(16)	56(1)	42(1)	46(1)	4(1)	3(1)	-10(1)
C(17)	59(1)	48(1)	47(1)	2(1)	1(1)	-11(1)
C(18)	71(1)	49(1)	49(1)	0(1)	8(1)	-14(1)
C(19)	69(1)	44(1)	59(1)	1(1)	19(1)	-8(1)
C(20)	57(1)	52(1)	63(1)	8(1)	6(1)	-2(1)
C(21)	61(1)	52(1)	48(1)	4(1)	2(1)	-4(1)
N(1)	56(1)	55(1)	46(1)	-2(1)	3(1)	-4(1)
N(2)	51(1)	59(1)	46(1)	-3(1)	2(1)	-7(1)
N(17)	63(1)	74(1)	56(1)	-4(1)	-6(1)	-10(1)
N(19)	81(1)	55(1)	81(1)	0(1)	30(1)	-7(1)
O(171)	57(1)	103(1)	70(1)	-8(1)	-3(1)	0(1)
O(172)	95(1)	176(2)	66(1)	-38(1)	-24(1)	16(1)
O(191)	79(1)	86(1)	116(1)	-9(1)	31(1)	6(1)
O(192)	123(1)	85(1)	74(1)	-13(1)	38(1)	-1(1)

TABLE 3

H(3)	1250(1)	030(2)	-233(1)	56(4)
H(41)	1129(2)	-244(3)	-305(1)	70(6)
H(42)	1150(2)	-057(4)	-337(1)	102(7)
H(51)	1343(2)	-083(4)	-318(1)	105(8)
H(52)	1285(2)	-280(4)	-347(1)	120(9)
H(7)	1445(2)	-072(4)	-237(1)	95(7)
H(81)	1460(2)	-398(4)	-152(1)	107(8)
H(82)	1558(2)	-251(4)	-161(1)	108(8)
H(10)	1288(1)	-237(3)	-142(1)	59(5)
H(11)	1290(2)	136(3)	-113(1)	76(6)
H(121)	954(2)	-066(4)	-208(1)	111(9)
H(122)	1010(2)	-277(5)	-205(1)	125(10)
H(123)	985(2)	-161(3)	-262(1)	85(6)
H(131)	1344(2)	-546(4)	-214(1)	127(10)
H(132)	12354(2)	-462(4)	-231(1)	123(9)
H(133)	1284(2)	-543(5)	-283(2)	144(12)
H(141)	1478(2)	110(3)	-153(1)	92(7)
H(142)	1571(2)	031(4)	-102(1)	110(8)
H(143)	1470(2)	145(5)	-080(1)	135(10)
H(151)	1436(2)	-365(4)	-059(1)	94(7)
H(152)	1443(2)	-154(5)	-024(1)	136(11)
H(153)	1553(2)	-272(3)	-050(1)	104(8)
H(18)	1028(2)	344(3)	101(1)	72(5)
H(20)	799(1)	334(3)	-037(1)	59(5)
H(21)	915(2)	187(3)	-093(1)	86(6)
H(N2)	1172(2)	087(3)	-048(1)	64(5)

TABLE 4

C(1) - C(2)	1.481(2)	C(10) - C(11)	1.317(3)
C(1) - C(11)	1.486(2)	C(16) - C(17)	1.425(2)
C(1) - N(1)	1.290(2)	C(16) - C(21)	1.422(2)
C(2) - C(3)	1.331(2)	C(16) - N(2)	1.336(2)
C(2) - C(12)	1.499(3)	C(17) - C(18)	1.377(2)
C(3) - C(4)	1.493(3)	C(17) - N(17)	1.444(2)
C(4) - C(5)	1.546(3)	C(18) - C(19)	1.366(2)
C(5) - C(6)	1.505(3)	C(19) - C(20)	1.392(2)
C(6) - C(7)	1.342(3)	C(19) - N(19)	1.457(2)
C(6) - C(13)	1.488(4)	C(20) - C(21)	1.358(2)
C(7) - C(8)	1.502(3)	N(1) - N(2)	1.379(2)
C(8) - C(9)	1.562(3)	N(17) - O(171)	1.229(2)
C(9) - C(10)	1.511(2)	N(17) - O(172)	1.222(2)
C(9) - C(14)	1.524(4)	N(19) - O(191)	1.221(2)
C(9) - C(15)	1.534(4)	N(19) - O(192)	1.221(2)

TABLE 5

C(11) - C(1) - C(2)	117.4(1)		N(1) - C(1) - C(2)	118.3(1)
C(3) - C(2) - C(1)	118.3(1)		C(12) - C(2) - C(1)	118.0(1)
N(1) - C(1) - C(11)	124.2(1)		C(10) - C(11) - C(1)	120.9(2)
N(2) - N(1) - C(1)	114.2(1)		C(12) - C(2) - C(3)	123.8(2)
C(4) - C(3) - C(2)	128.5(2)		C(5) - C(4) - C(3)	109.6(2)
C(6) - C(5) - C(4)	111.9(2)		C(7) - C(6) - C(5)	119.8(2)
C(13) - C(6) - C(5)	115.5(2)		C(13) - C(6) - C(7)	124.4(2)
C(8) - C(7) - C(6)	127.0(2)		C(9) - C(8) - C(7)	113.3(2)
C(10) - C(9) - C(8)	106.3(2)		C(14) - C(9) - C(8)	111.1(2)
C(15) - C(9) - C(8)	108.9(2)		C(14) - C(9) - C(10)	111.7(2)
C(15) - C(9) - C(10)	109.2(2)		C(11) - C(10) - C(9)	129.4(2)
C(15) - C(9) - C(14)	109.5(2)		C(21) - C(16) - C(17)	116.1(1)
N(2) - C(16) - C(17)	123.3(1)		C(18) - C(17) - C(16)	121.6(1)
N(17) - C(17) - C(16)	121.6(1)		N(2) - C(16) - C(21)	120.5(1)
C(20) - C(21) - C(16)	121.6(2)		N(1) - N(2) - C(16)	120.7(1)
N(17) - C(17) - C(18)	116.8(1)		C(19) - C(18) - C(17)	119.5(1)
O(171) - N(17) - C(17)	119.6(1)		O(172) - N(17) - C(17)	118.5(2)
C(20) - C(19) - C(18)	121.2(2)		N(19) - C(19) - C(18)	118.6(2)
N(19) - C(19) - C(20)	120.1(2)		C(21) - C(20) - C(19)	119.9(2)
O(191) - N(19) - C(19)	117.4(2)		O(192) - N(19) - C(19)	119.0(2)
O(172) - N(17) - O(171)	121.9(2)		O(192) - N(19) - O(191)	123.6(2)

TABLE 6

C(11)	C(1)	C(2)	C(3)	-25.6(2)	C(11)	C(1)	C(2)	C(12)	153.4(2)
N(1)	C(1)	C(2)	C(3)	157.4(2)	N(1)	C(1)	C(2)	C(12)	-23.6(2)
C(2)	C(1)	C(11)	C(10)	-52.2(2)	N(1)	C(1)	C(11)	C(10)	124.6(2)
C(2)	C(1)	N(1)	N(2)	174.2(1)	C(11)	C(1)	N(1)	N(2)	-2.5(2)
C(1)	C(2)	C(3)	C(4)	167.5(2)	C(12)	C(2)	C(3)	C(4)	-11.4(3)
C(2)	C(3)	C(4)	C(5)	-140.6(2)	C(3)	C(4)	C(5)	C(6)	46.1(2)
C(4)	C(5)	C(6)	C(7)	-105.2(2)	C(4)	C(5)	C(6)	C(13)	68.8(3)
C(5)	C(6)	C(7)	C(8)	167.1(2)	C(13)	C(6)	C(7)	C(8)	-6.3(4)
C(6)	C(7)	C(8)	C(9)	-107.4(3)	C(7)	C(8)	C(9)	C(10)	47.6(2)
C(7)	C(8)	C(9)	C(14)	-74.1(3)	C(7)	C(8)	C(9)	C(15)	165.2(2)
C(8)	C(9)	C(10)	C(11)	-135.6(2)	C(14)	C(9)	C(10)	C(11)	-14.3(3)
C(15)	C(9)	C(10)	C(11)	107.0(3)	C(9)	C(10)	C(11)	C(1)	171.5(2)
C(21)	C(16)	C(17)	C(18)	-2.7(2)	C(21)	C(16)	C(17)	N(17)	178.1(1)
N(2)	C(16)	C(17)	C(18)	176.4(2)	N(2)	C(16)	C(17)	N(17)	-2.9(2)
C(17)	C(16)	C(21)	C(20)	2.4(2)	N(2)	C(16)	C(21)	C(20)	-176.7(2)
C(17)	C(16)	N(2)	N(1)	177.2(1)	C(21)	C(16)	N(2)	N(1)	-3.7(2)
C(16)	C(17)	C(18)	C(19)	0.8(2)	N(17)	C(17)	C(18)	C(19)	-180.0(2)
C(16)	C(17)	N(17)	O(171)	-0.5(2)	C(16)	C(17)	N(17)	O(172)	-179.1(2)
C(18)	C(17)	N(17)	O(171)	-179.9(2)	C(18)	C(17)	N(17)	O(172)	1.6(2)
C(17)	C(18)	C(19)	C(20)	1.6(3)	C(17)	C(18)	C(19)	N(19)	-176.0(2)
C(18)	C(19)	C(20)	C(21)	-1.8(3)	N(19)	C(19)	C(20)	C(21)	175.7(2)
C(18)	C(19)	N(19)	O(191)	171.2(2)	C(18)	C(19)	N(19)	O(192)	-7.3(3)
C(20)	C(19)	N(19)	O(191)	-6.4(3)	C(20)	C(19)	N(19)	O(192)	175.2(2)
C(19)	C(20)	C(21)	C(16)	-0.2(3)	C(1)	N(1)	N(2)	C(16)	170.7(1)

TABLE 7

C(3) - H(3)	0.990(18)
C(4) - H(41)	1.04(2)
C(4) - H(42)	1.01(3)
C(5) - H(51)	1.04(3)
C(5) - H(52)	1.05(3)
C(7) - H(7)	1.04(3)
C(8) - H(81)	1.07(3)
C(8) - H(82)	0.99(3)
C(10) - H(10)	0.976(19)
C(11) - H(11)	0.93(2)
C(12) - H(121)	0.94(3)
C(12) - H(122)	1.06(3)
C(12) - H(123)	0.95(2)
C(13) - H(131)	0.97(3)
C(13) - H(132)	1.04(3)
C(13) - H(133)	1.01(4)
C(14) - H(141)	1.03(2)
C(14) - H(142)	0.92(3)
C(14) - H(143)	1.16(3)
C(15) - H(151)	1.03(3)
C(15) - H(152)	1.10(3)
C(15) - H(153)	1.02(3)
C(18) - H(18)	0.95(2)
C(20) - H(20)	0.917(19)
C(21) - H(21)	0.99(2)
N(2) - H(N2)	0.84(2)

For the 11-membered ring :

H-Csp^2-Csp^3 valence angles range from 113.4(11)° to 117.5(13)°.

H-Csp^2-Csp^2 valence angles range from 114.4(13)° to 122.4(13)°.

H-Csp^3-Csp^2 valence angles range from 105.9(14)° to 118.8(18)°.

H-Csp^3-Csp^3 valence angles range from 103.5(14)° to 113.3(16)°.

H-Csp^3-H valence angles range from 98.8(24)° to 117.1(21)°.

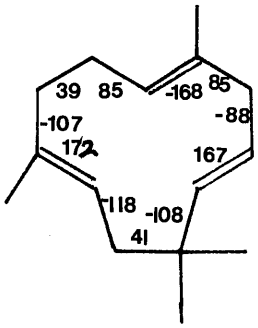
For the dinitrobenzoate ring :

H-Csp^2-Csp^2 valence angles range from 118.6(12)° to 124.5(12)°.

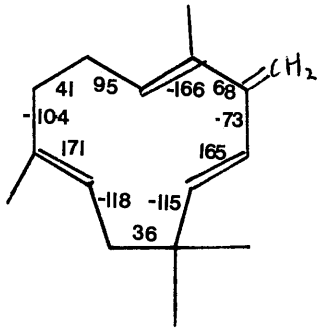
H(N2)-N2-N1 121.1(13)° H(N2)-N2-C16 118.0(13)°

FIG. 4.5 V_S in kcal./mole
TAs in (°)

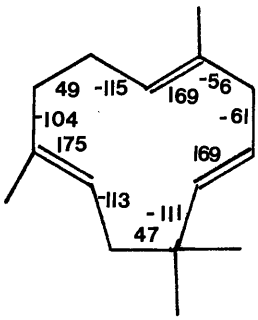
H I
V_S = 14.60



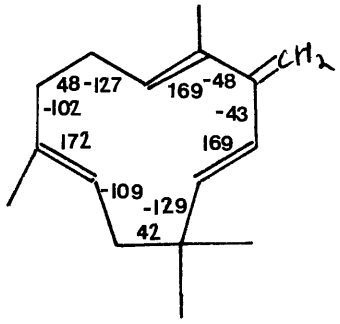
H II
V_S = 24.63



Z I
V_S = 13.45



Z II
V_S = 19.13



conformation Z is of lower energy than that of type H by 5.4 kcal $mole^{-1}$, while for humulene, the Z conformation is also the more stable, though by only 1.1 kcal $mole^{-1}$. Since the methylene compound should be a good analogue for zerumbone in force field calculations (compare force field calculations for cycloheptanone[29] and methylene cycloheptane[30]) it has been concluded that the dinitrophenylhydrazone group has not influenced the conformation of the macrocycle in the zerumbone 2,4-DNP. A breakdown of the components of V_s giving rise to the total V_s for each conformation is given in Table 7.

A Comparison of HI with ZI.

A close examination of the humulene conformations of type H and of type Z reveals that the major contributors to the steric energy in both cases are the van der Waals interactions, torsional strain and angle strain. This is as expected for medium-sized rings. The difference in energy between these conformations is 1.1 kcal $mole^{-1}$: almost half of this is due to increased angular strain in HI with respect to ZI; the rest results from equal contributions from torsional strain and out-of-plane bending. Large angle deviation is common in medium rings as it is less expensive energetically than torsional strain[33].

In both Z and H conformations, the angular strain results mainly from deviations from tetrahedral geometry around C_1: in ZI the C_2-C_1-C_{11} angle is 107° which is considerably less strained than the corresponding HI angle of 103°. In both conformations, torsional strain is greatest around Csp^3-Csp^2-Csp^2-Csp^3 sites: changes in these TAs result not only from twisting around the central bond but also from out-of-plane bending at trigonal atoms. Both conformations exhibit transannular interactions between C_3 and C_6; C_7 and C_{10}; C_7 and a C_5 hydrogen and between hydrogens on C_4 and C_{12}.

TABLE 7 : All values given in kcal $mole^{-1}$.

	HI	ZI	HII	ZII
V_b	0.76	0.73	0.83	0.81
V_r	5.60	5.46	6.39	6.77
V_a	2.49	1.98	2.59	2.57
V_w	5.16	4.90	14.13	8.67
V_x	0.59	0.38	0.69	0.31
V_s	14.60	13.45	24.63	19.13

An ORTEP representation[20,28] for HI is given in Figure 4.6 and for ZI in Figure 4.7. In these 11-membered rings, the methyl groups on C_2 and C_6 are on opposite faces of the mean molecular plane. It has been found[34-37], that in a number of germacranolides containing 10-membered rings with trans double bonds or epoxide functions, these methyl groups are on the same side of the mean molecular plane.

Mean molecular plane calculations for both conformations (H and Z) of humulene are listed in Table 8.

Figure 4.8 indicates that both conformations differ in only part of the ring system. Using the "congest" option of the GUCGS[28] the outcome of stereoselective attack at trigonal atoms is predicted: in HI, double bonds C_6=C_7 and C_{10}=C_{11} prefer to be attacked from above the mean plane of the ring while attack at the C_2=C_3 centre is preferentially from below the mean plane. In ZI, all three double bonds prefer to be attacked from the same side of the ring. In both H and Z, C_2 ....C_{10}, and C_3 ....C_{11} distances are ca. 3Å: if epoxidation of both these double bonds occurs from the same side of the ring, oxygen atoms will be very close. This would give rise to very large, unfavourable van der Waals interactions. These calculations suggest that epoxidation of humulene would occur preferentially for conformation H rather than for Z.

Shirahama[38] and coworkers have recently investigated humulene conformations via force field calculations on the four stable conformations envisaged from inspection of molecular models. These conformations are indicated in Figure 4.9: the C and T notation[39] denotes "crossed" and "parallel" arrangements of two double bonds in 1,5-diene systems. Humulene contains two such systems. They predict that the CT and CC conformation are significantly more stable than the others. The CT conformation is the same as that found in the humulene-$AgNO_3$ complex and in the calculated HI conformation. The CC conformation corresponds to the zerumbone 2,4-DNP derivative and

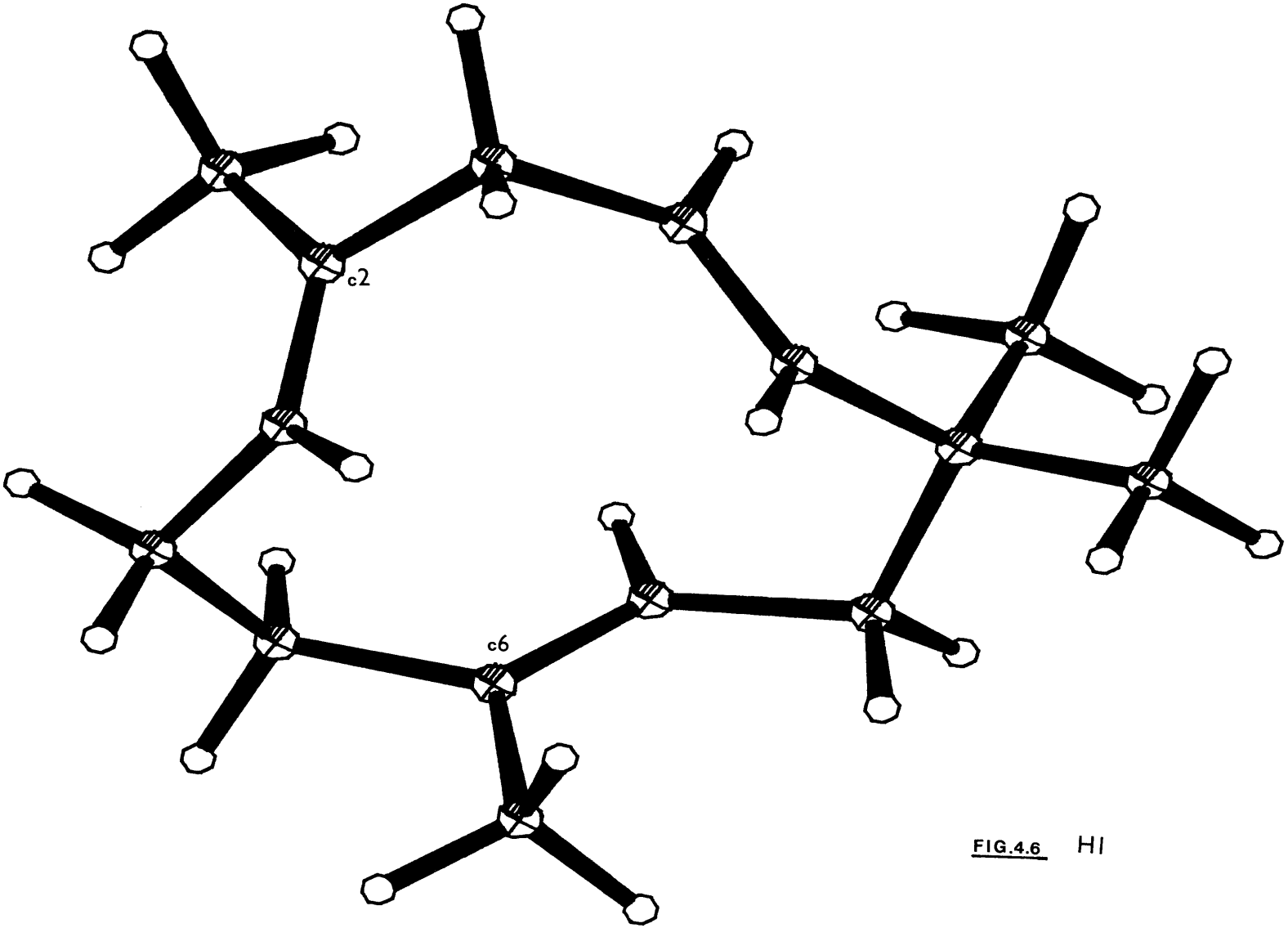


FIG.4.6 HI

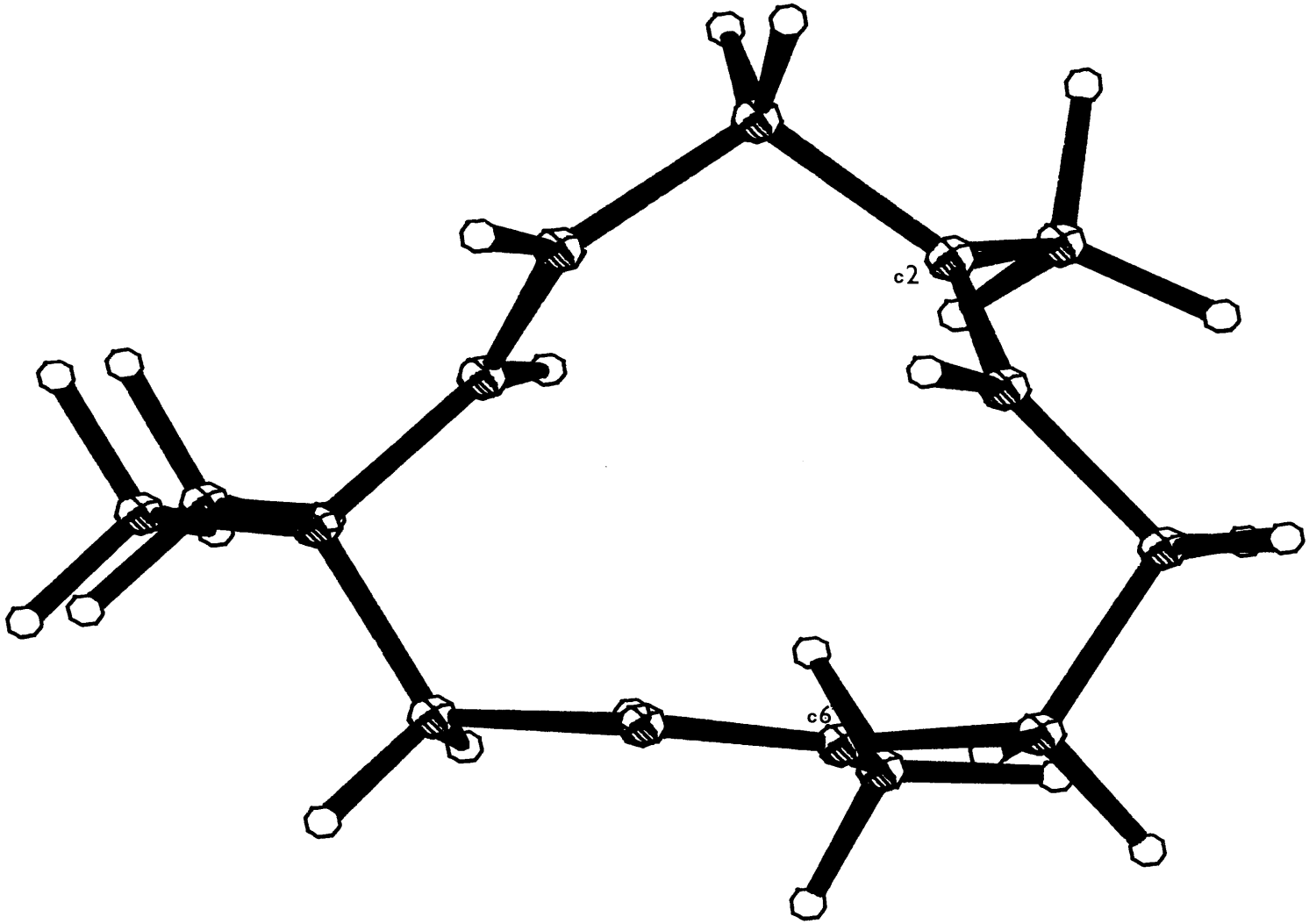


FIG. 4.7 ZI

TABLE 8 : all deviations from the planes are given in Å.

	ATOM	ZI	HI
Plane 1:	C9	0.075	-0.088
	C10	-0.039	0.048
	C11	-0.040	0.049
	C1	0.077	-0.090
	H10	-0.039	0.043
	H11	-0.034	0.038
Plane 2:	C5	-0.039	0.058
	C6	0.017	-0.025
	C7	0.021	-0.029
	C8	-0.039	0.059
	C13	0.016	-0.026
	H7	0.024	-0.03
Plane 3:	C1	0.081	0.081
	C2	-0.036	-0.045
	C3	-0.041	-0.047
	C4	0.081	0.081
	C12	-0.033	-0.026
	H3	-0.052	-0.045

Angle between normals to planes (°):

1 and 2	48	45
1 and 3	98	93
2 and 3	51	137

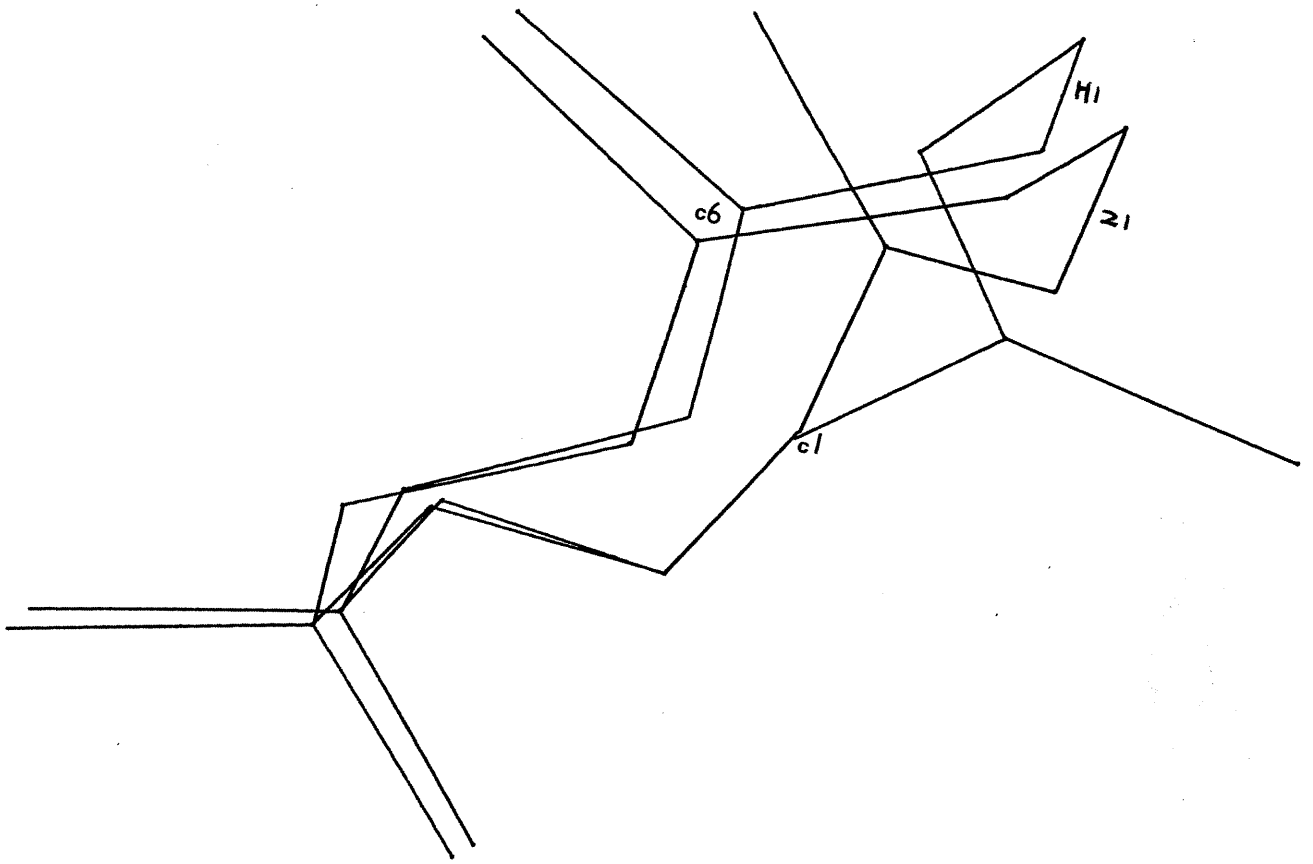
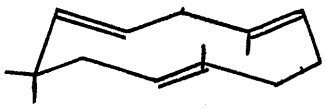
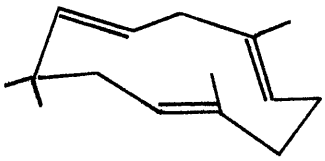


FIG. 4.8 H1 with Z1

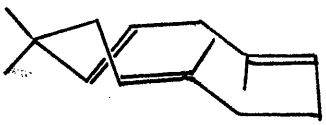
FIG. 4.9



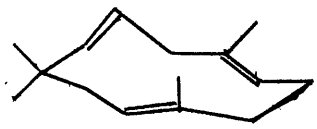
CT



CC



TT

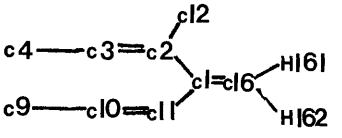


TC

the calculated ZI conformation. Torsion angles for these systems are recorded in Table 9.

A Comparison of HII and ZII

From Table 7, it is clear that both zerumbone conformations, HII and ZII, possess considerable torsional strain, van der Waals interaction energy and, to a lesser degree, angle strain. Conformation of type H is 5.4 kcal $mole^{-1}$ higher in energy than conformation of type Z: 99% of this increased strain energy in HI, arises from greater torsional strain around the fragment of the ring indicated below:



TA distortion and out-of-plane bending is greatest for the unsubstituted C_{10}, C_{11} trigonal atoms : echoing the situation in costunolide and other germacranolides[40].

In both HII and ZII, maximum overlap of pi orbitals would be achieved by a planar arrangement of the above fragment. However, a completely planar conformation would have very large transannular interactions - especially between hydrogens on C_3 and C_{10}. Table 10 lists mean plane calculations for both conformations: these results suggest that conformation ZII requires less twisting around the C_1-C_{11} and C_1-C_2 bonds to relieve steric crowding and transannular interactions. Figure 4.10 reveals that both conformations differ around the C_2-C_3-C_4-C_5 section of the ring. ORTEP[20,28] representations of HII and ZII are given in Figures 4.11 and 4.12 respectively.

In order to consider the conjugation in HII and ZII it is useful to refer to butadiene - this is believed to exist in two stable (or metastable) conformations[41] called "s-trans" and

TABLE 9 : All TAs given in (°).

TA	$AgNO_3$[11]	HI	CT[38a]	Z2,4DNP	ZI	CC[38]
5-6=7-8[b]	-172	-172	-173	-167	-175	-174
4-5-6-7	109	107	105	105	104	105
3-4-5-6	-35	-39	-45	-46	-49	-45
2-3-4-5	-77	-85	-81	141	115	125
1-2=3-4	162	168	168	-168	-169	-174
11-1-2-3	-95	-85	-84	26	56	45
10-11-1-2	94	88	89	52	62	58
9-10=11-1	-156	-167	-168	-171	-169	-174
8-9-10-11	102	108	107	136	111	121
7-8-9-10	-55	-41	-40	-48	-47	-44
6-7-8-9	126	118	127	107	113	110

a : calculated using Allinger's[39] force field.

b : = signifies a double bond.

TABLE 10 : all deviations from the planes are given in Å.

	ATOM	HII	ZII
Plane 1:	C1	-0.104	0.081
	C2	0.048	-0.032
	C3	0.049	-0.034
	C4	-0.103	0.080
	C12	0.041	-0.036
	H3	0.069	-0.059
Plane 2:	C5	0.066	-0.057
	C6	-0.029	0.027
	C7	-0.033	0.031
	C8	0.067	-0.058
	C13	-0.029	0.022
	H7	-0.042	0.034
Plane 3:	C9	-0.112	0.084
	C10	0.050	-0.033
	C11	0.053	-0.030
	C1	-0.115	0.080
	H10	0.066	-0.064
	H11	0.058	-0.049
Plane 4:	C1	-0.020	-0.005
	C16	-0.003	-0.001
	C11	0.007	0.004
	C2	0.008	0.001
	H161	0.004	0.001
	H162	0.004	0.001

Angles between normals to the planes (°):

1,2	40	57
1,3	76	109
1,4	110	129
2,3	43	52
2,4	95	83
3,4	104	45

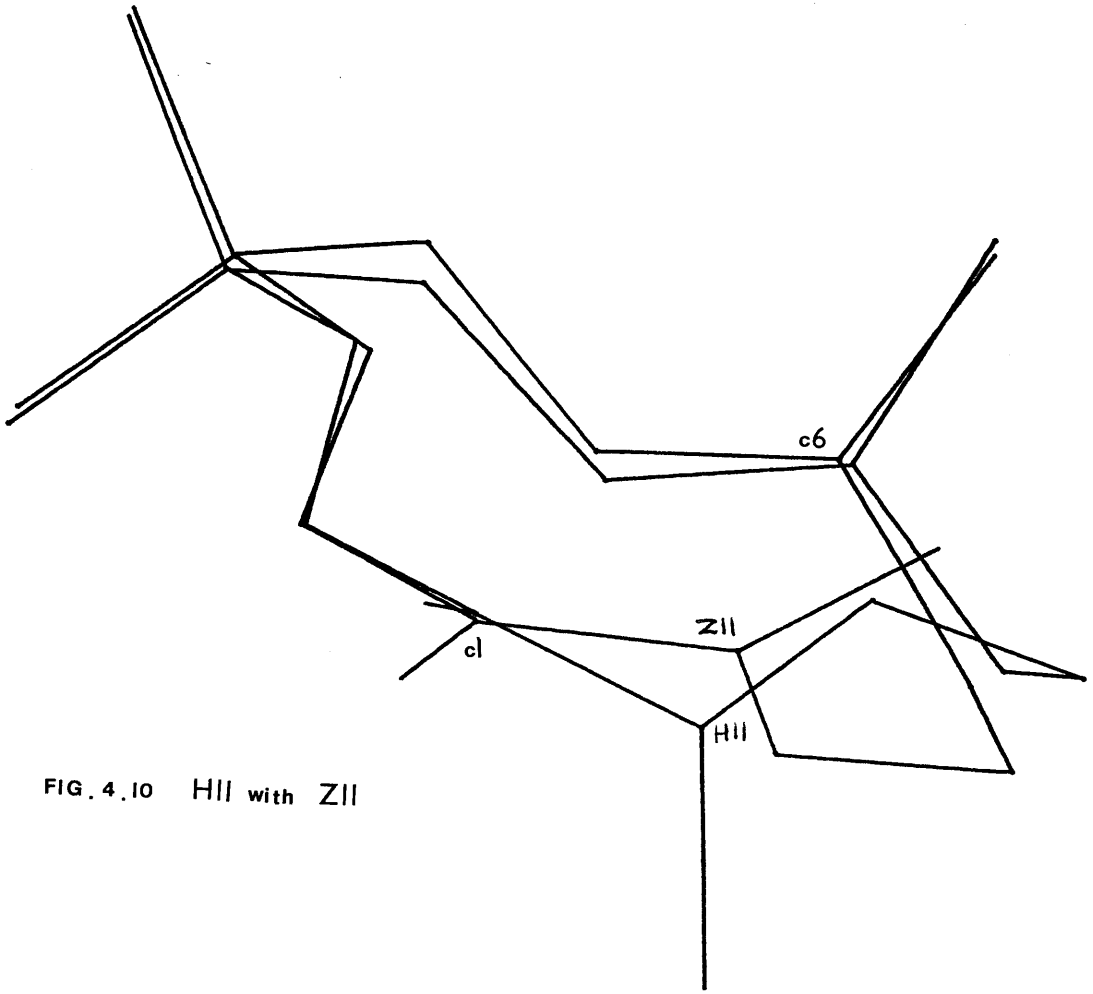


FIG. 4.10 H11 with Z11

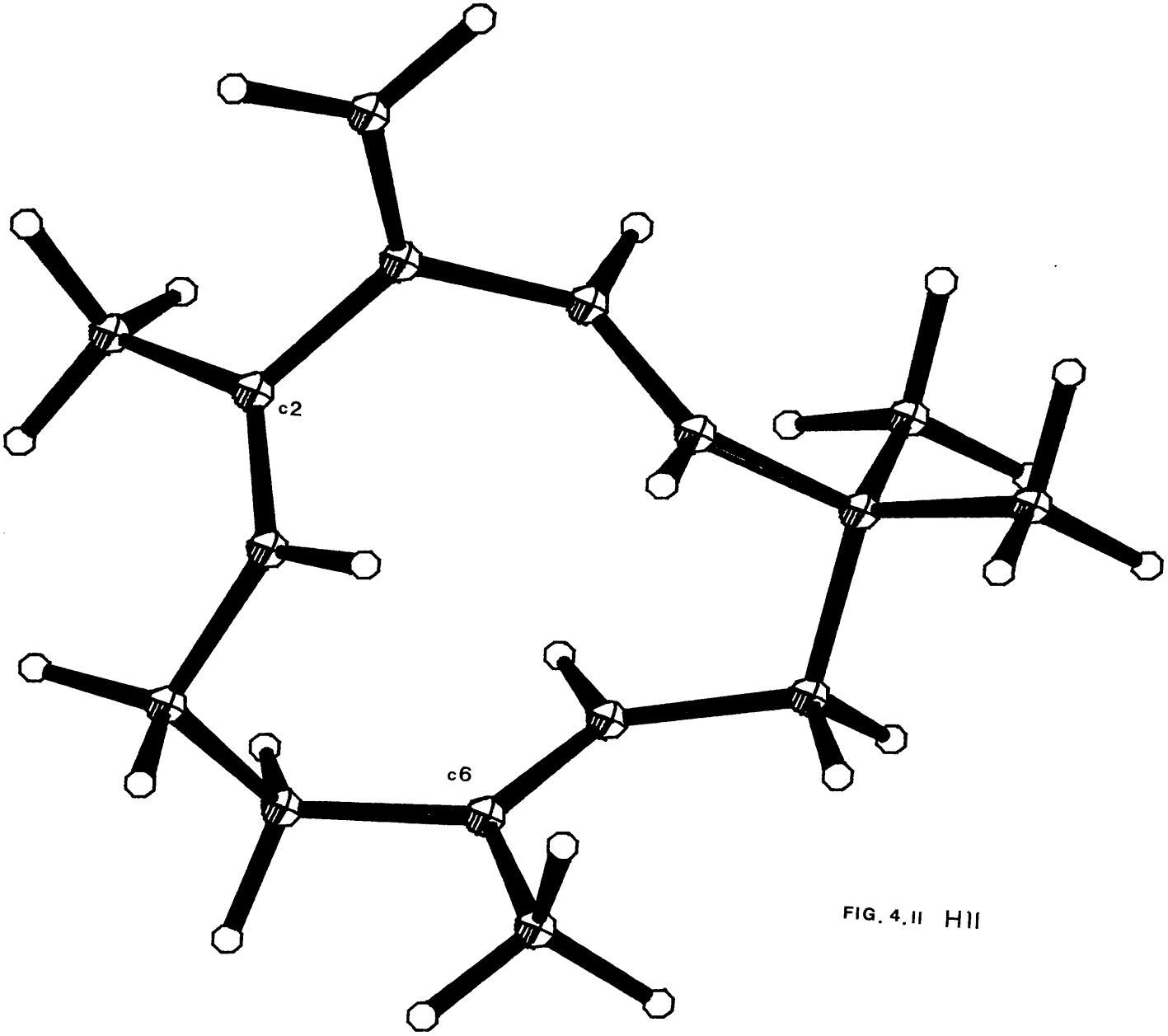


FIG. 4.11 H11

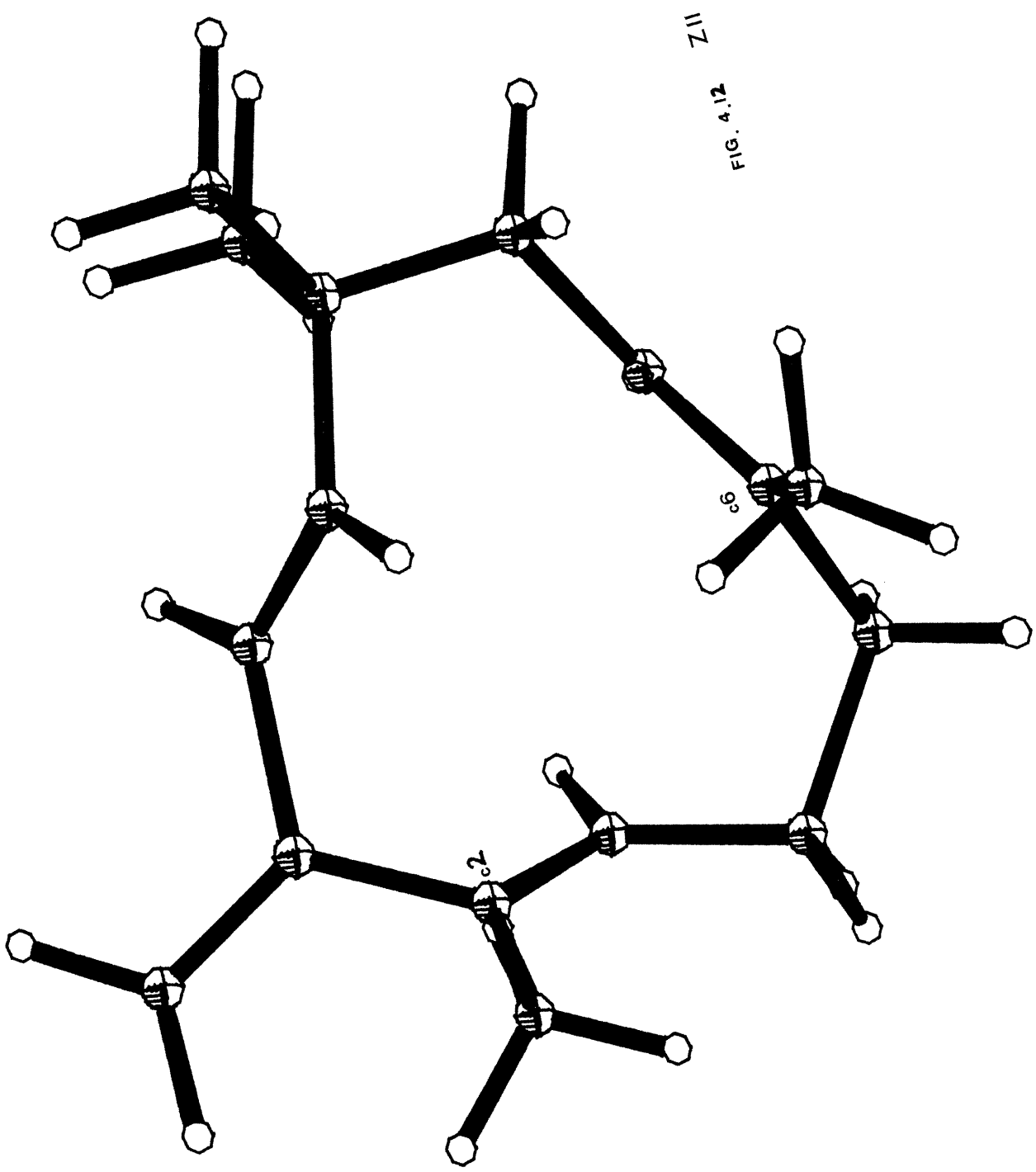
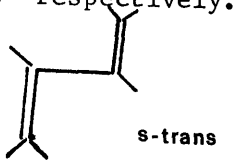
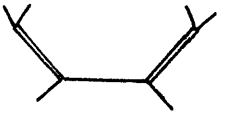


FIG. 4.12 Z11

"s-cis" respectively. These forms are now indicated.





The s-trans form is calculated to be the more stable[42]. A similar situation is found in α,β-unsaturated ketones. Homoannular representatives such as cholest-4-en-3-one are s-trans and the heteroannular representatives such as cholest-4-en-3-ol-6-one are s-cis. HII and ZII may be considered as homoannular dienes with an exocyclic double bond. The TAs for this conjugated segment for both conformations are listed in Table 11:

TABLE 11 : All TAs are given in (°).

TA	HII	ZII
16-1-2-3	-115	130
16-1-2-12	71	-53
16-1-11-10	110	138
16-1-11-H_{11}	-77	-46

Conformation ZII is more transoid than the HII, however, both conformations may be skewed from s-trans configurations in order to minimise transannular interactions between hydrogens on C_{10} and C_3.

In conclusion, therefore, the ZII conformation is calculated to be the more stable one as a result of decreased torsional strain around the conjugated section of its structure.

A Comparison of ZI with ZII, and of HI with HII.

From examination of ZI with respect to ZII, and of HI in relation to HII, both humulene conformations are found to be of

lower energy than the zerumbone conformations. In both comparisons, the large increase in steric energy when moving from the humulenes to the zerumbones is a result of the introduction of considerable Pitzer strain around the conjugated section of ZII and HII.

Introduction of a sp^2-carbon instead of a sp^3-carbon has imposed planarity around the conjugated section of the ring for maximum pi orbital overlap and most stability. Neither HII nor ZII are completely planar. The resulting TAs have far from ideal values, thereby increasing the torsional strain of both systems with respect to their humulene analogues in which no such condition for planarity has been imposed.

A conformation with three double bonds involved in conjugation and sharing a common plane is unlikely - such a conformation would contain very unfavourable transannular interactions. ZII represents a conformation in which a better compromise has been reached: the ring double bonds are twisted in opposite directions from the plane established by the exocyclic double bond, in an effort to relieve these repulsive interactions.

The increased Pitzer strain in ZII, with respect to ZI, is relieved somewhat by a less costly increase in angular strain in terms of energy: this is not seen to happen for HII. The C_9-C_{10}=C_{11} angle has moved from a value of 126° in ZI to a more strained value of 127° in ZII: in both HI and HII, this angle has a value of 125°.

4.5 DISCUSSION OF RESULTS.

The molecular structure of zerumbone 2,4-dinitrophenylhydrazone is given in Figure 4.4, confirming that all three double bonds in the 11-membered ring have trans stereochemistry. The TAs around the C-C bonds of the 11-membered ring in this structure are given in Table 12 (column Z), together with the values for humulene in its $AgNO_3$ complex[11] (column H). The conformations are seen to differ in the region of the phenylhydrazone group of the zerumbone derivative.

The cycloundecatriene conformation in zerumbone 2,4-DNP has approximate C_2 symmetry, the only notable departure being evident in the TAs around bonds C_1-C_2, -26°, and C_1-C_{11}, -52°. The larger angle of this pair probably arises from the need to keep the C_{11}-hydrogen and N-hydrogen atoms apart (H....H 2.31 Å). In the methylene analogue, ZII, this deviation disappears.

The conformation found for the 11-membered ring in zerumbone 2,4-DNP is quite different from that characterised in a low temperature x-ray study of cycloundecanone[43]; on the other hand, it resembles a conformation found for cycloundec-1-ene carboxylic acid (column E in Table 12) which will be discussed in the following chapter. Included in Table 12 are the force field results for HI (column HI) and for ZII (column ZII).

The four C-Csp^3-C angles in the 11-membered ring in zerumbone 2,4-DNP range from 106° to 113° and the six C-C=C angles range from 118° to 129°. The force field calculations for ZII reproduce these variations in a most satisfactory manner. (See Table 13).

MM calculations suggest that in humulene, there is preferential attack of the C_2=C_3 and C_{10}=C_{11} double bonds from opposite sides of the ring while in zerumbone, attack of these

TABLE 12 : All TAs are in (°).

TA	Z	H	E	ZII	HI
	[--observed--]			[-calculated-]	
11-1-2-3	-26	95	-80	-48	85
1-2=3-4	168	-162	155	170	-168
2-3-4-5	-141	77	-90	-127	85
3-4-5-6	46	35	63	48	39
4-5-6-7	-105	-109	-111	-102	-107
5-6=7-8	167	172	178	172	172
6-7-8-9	-107	-126	-116	-110	-118
7-8-9-10	48	55	54	42	41
8-9-10-11	-136	-102	-94	-129	-108
9-10=11-1	172	156	155	169	167
10-11-1-2	-52	-94	-70	-43	-88

TABLE 13 : All valence angles are in (°).

ANGLE	Z_{obs}	ZII_{calc}
11-1-2	117.4	114.8
1-2-3	118.3	118.3
2-3-4	128.5	128.4
3-4-5	109.6	110.0
4-5-6	111.9	112.6
5-6-7	119.8	120.3
6-7-8	127.0	126.7
7-8-9	113.3	112.8
8-9-10	106.3	107.6
9-10-11	129.4	127.3
10-11-1	120.9	120.5

double bonds would occur on the same side of the ring. This suggests a possible explanation for the existence of the humulene conformation as opposed to the zerumbone conformation in the di- and tri-epoxides i.e. HI is preferred to ZI as the latter would suffer steric hindrance from the lone pairs on oxygen atoms occupying the $C_2=C_3$ and $C_{10}=C_{11}$ double bonds. Similarly, in the $AgNO_3$ complex of humulene, conformation ZI would require both Ag^+ ions to be on the same side of the ring while conformation HI would place them on opposite sides.

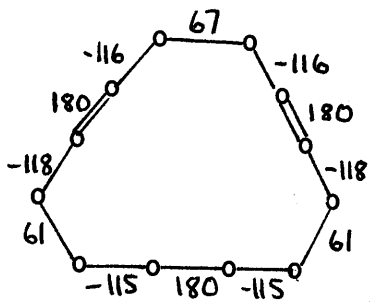
In zerumbone, the calculated lower energy conformation is the one observed.

Further evidence that the favoured conformation of humulene is of type Z rather than type H can be seen by comparing these conformations with the observed crystal structure of the all-trans cyclododeca-1,5,9-triene[44] as indicated in Figure 4.13. Dale[33] has predicted that with three double bonds in a ring, "trigonal" ideal conformations with symmetrically placed trans double bonds become possible - his predicted conformation for the all-trans cyclododeca-1,5,9-triene matches that of the experimental analysis. Both HI and ZI have main features in common with the 12-membered ring, but ZI more closely follows the signs of the TAs than HI; most of the strain in the 11-membered ring is located in that part of the ring where one CH_2 group is missing.

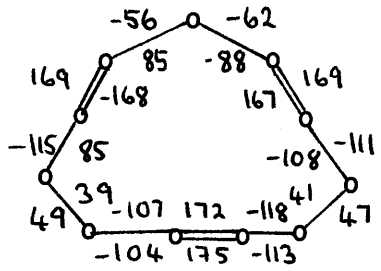
There is a large measure of correspondence between conformations H and Z . The indication that the energetically favoured conformation of humulene may be of type Z rather than type H does not require any revision of previous proposals, that the stereochemistries of various sesquiterpenoids are consistent with biogenesis from humulene-like precursors. Shirahama[38] and his associates confirm this view. They believe that if their conformations CT (HI) and CC (ZI) are kept approximately unchanged through reactions to the illudoids, the existence of two biosynthetic pathways can be implied, instead of assuming a

FIG. 4.13

All TAs in (°)



Cyclododeca-1,5,9-triene[4]



Internal values - HI

External values - ZI

single route i.e. CT --> protoilludane and CC --> hirsutane instead of CT --> protoilludane --> hirsutane. (See Figure 4.1).

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CHAPTER FIVE

AN X-RAY ANALYSIS OF DIMETHYL (8'-DIMETHYLAMINONAPHTHYL) AMMONIUM DIHYDROGEN TRIS(CYCLOUNDEC-1-ENE CARBOXYLATE). AN ACID SALT OF THE TYPE $BH^+.X^-.2HX$.

5.0 FOREWORD

The 8- to 11-membered rings[1] are called the medium rings and distinguish themselves by special properties in their conformations. In general, it can be said that the physical and chemical properties of the medium rings show decided maxima or minima[2-4] - they are no longer monotonic functions of the numbers of carbons in the ring. Until quite recently, however, the necessary structural data were not available, so that initial attempts[5] to interpret the chemical properties of medium rings were based on considerations derived from working models. The enormous variety of possible conformations and the lack of any quantitative criteria for deciding between them made it practically impossible to derive actual molecular conformational maps.

The last twenty years has seen a considerable accumulation of information on the conformations of medium rings. The experimental evidence comes mainly from x-ray analyses of suitable crystalline derivatives but also from spectral studies. Attempts to predict the conformations of medium rings by strain energy minimisation calculations have become more refined with the availability of faster computers with greatly increased storage space.

There remains, however, a distinct lack of structural and conformational information for the 11- and higher odd-membered rings. To reduce this imbalance a little, several crystalline derivatives of 11-membered ring compounds have been prepared and examined. The previous chapter dealt with the triply unsaturated 11-membered ring derivative of zerumbone. This chapter deals with a mono-unsaturated 11-membered ring derivative, namely, dimethyl (8′-dimethylaminonaphthyl) ammonium dihydrogen tris(cycloundec-1-ene carboxylate).

5.1 AN INTRODUCTION TO ACID SALTS AND HYDROGEN BONDING.

In the solid state, many substances appear to crystallise in such a way that the packing of the molecules approaches some kind of close packing. If the van der Waals radii of the molecules are constant then the deciding issue appears to be efficient space filling by these molecular groups. There are, however, a number of rather specific intermolecular interactions which can influence the packing significantly. By far the most ubiquitous and widely studied specific intermolecular interaction which affects the structure of condensed states is that known as the "hydrogen bond".

The concept of the hydrogen (or H) bond was first introduced by Latimer and Rodebush[6] in 1920. Since then, there has been considerable discussion of a suitable definition of the hydrogen bond. The distinguishing feature of H bonding is the involvement of a specific H atom of a proton donor group with a localised site of high electron density in the same or another molecule. In other words, between molecule A-H and a second atom or molecule, B, a specific force may operate which is much weaker than the covalent bond A-H and is represented by A-H....B.

General evidence for such bonding comes from many sources and one of the earliest was the recognition that water is a most unusual compound. For example, with so low a relative molecular mass, one would expect water to be a gas, yet it has a boiling point of ca. 100°C higher than any other substance of a comparable molecular weight. This and many other anomalies were explained by the notion that liquid water is "associated" i.e. that its molecules contrive to cluster together. It was concluded that the hydrogen atom must be directly involved in this association.

There are important cases of H bonding where the two bonds to hydrogen are equal in strength and length. Among the known

examples are F-H-F in the difluoride ion and O-H-O in the acid salts of several monobasic acids.

The criteria for the existence of H bonds are somewhat more clear cut than for other intermolecular interactions. However, no single criterion or single physical manifestation can establish the presence of H bonding in a given system beyond any reasonable doubt. Some convenient operational criteria for the existence of H bonding are now listed:

1. H bonding occurs between a proton donor group, A-H, and a proton acceptor group, B, where A is an electronegative atom and the acceptor group is a lone electron pair of an electronegative atom or a pi-electron orbital of a multiple bond. Generally, an H bond can be characterised as a proton shared by two lone electron pairs.
2. H bonding is a distinctly directional and specific interaction. H bonds are approximately linear but appreciable variation in the angle A-H-B can occur.
3. The total H bond length r(A....B) is equal to, or less than, the sum of the van der Waals radii of atoms A and B i.e. the total bond length contraction caused by H bond formation is equal to, or greater than, twice the van der Waals radius of the hydrogen atom.

Two types of H bond complexes may be formed: intermolecular, involving two or more separate molecules; and intramolecular, involving donor and acceptor sites within the same molecule. The strength of H bonding depends on the relative acidities and basicities of the donor and the acceptor sites and, in the case of intramolecular H bonds, on the spatial arrangement present. An intramolecular H bond occurs only when the distance between the hydrogen of the donor group and the acceptor site is between 1.4 and 2.5 Å, and the angular orientation of the acceptor site does not deviate greatly from the bond axis of the donor group, A-H.

Experiment - mainly by x-ray diffraction - reveals O-H....O bonds with O....O in the range 2.4 to 3.2 Å. In the ranges, 3.2-2.8, 2.8-2.65 and 2.65-2.4 Å, the H bonds are known respectively, as long, medium and short. For N-H....N, the overall range is ca. 2.8-3.2 Å.

The potential energy of a diatomic molecule as a function of the distance between A and H, r(A-H), can be represented in two dimensions by a curve such as the one shown in Figure 5.1a. The minimum in the potential energy curve corresponds to the arbitrary energy zero on the ordinate, and to the equilibrium position of H in the A-H bond, (r_e) on the abcissa. The shape of the potential energy curve in an H bond A-H....B between two electronegative atoms A and B is very important to the understanding of spectroscopic manifestations of H bonding, the occurrence of proton transfer and other physical properties of H bonded molecules.

The bulk of the physicochemical evidence presently available indicates that the H atom is localised near the donor atom in the majority of H bonds, even when A and B are similar atoms. This situation is represented by an unsymmetrical potential energy curve (Figure 5.1b) where the lower of the two minima is located near the donor atom. The height of the second potential minimum was shown to depend on the strength of the proton donor and the acceptor strength of the base[7].

One of the early views of H bonding was the concept of mesomeric tautomerism, according to which, the H bond was thought to resonate very rapidly between two equally probable positions, one near the donor atom and the other near the acceptor atom. This concept would require that the potential energy function for the hydrogen atom either possess two equal potential minima with a low barrier between the two (Figure 5.1c), or be symmetrical, with one broad minimum (Figure 5.1d). Such cases are rare and they occur only in short, strong hydrogen bonds. Reliable

FIG. 5.1a

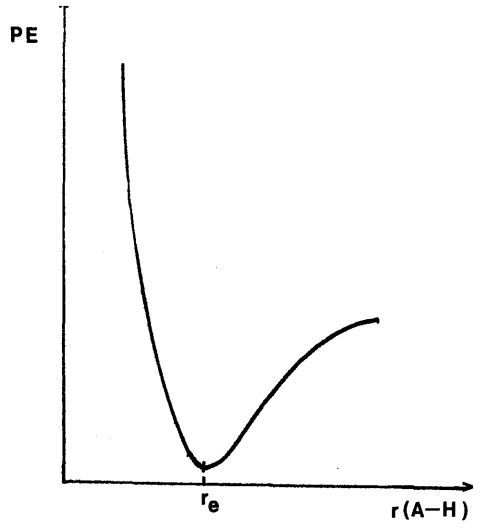


FIG. 5.1b

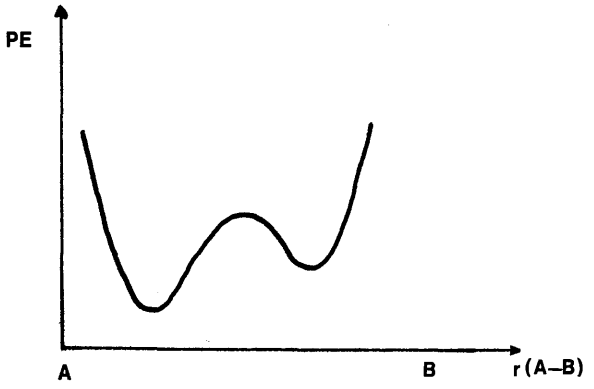


FIG. 5.1c

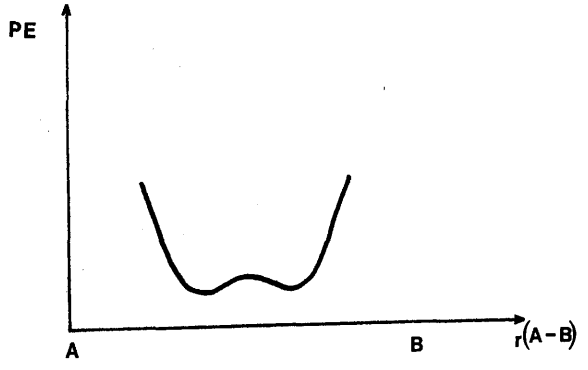
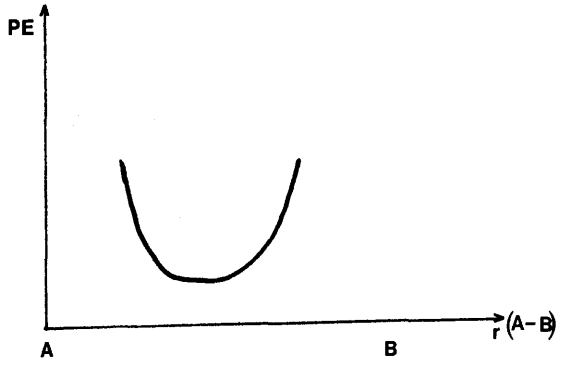


FIG. 5.1d



crystallographic evidence has been obtained for a symmetrical O′-H....O" bond in potassium hydrogen chloromaleate[8]. Most of the symmetrical H bonds known belong to this O′-H....O" type. They occur when r(O′....O") is 2.4-2.6 Å in the solid state.

A number of neutron diffraction investigations of the structure of various H bonded solids have been carried out in the last ten to fifteen years. Some of the results are presented in Tables 1 and 2[9-11]. Considerable attention has been devoted to compounds in which the presence of a symmetrical H bond, with either a single or double minimum, was suspected. The list of symmetrical O-H..O bonds is constantly growing[12] especially for the crystalline acid salts of carboxylic acids.

The chemical reaction that everybody knows and uses is that of an acid donating a proton to a base to form a salt: a monobasic acid, HX, forms a series of salts with a univalent cation, M^+, this series of salts is neutral and is represented by MX. From time to time, however, crystalline substances were discovered whose compositions corresponded to MHX_2. Anomalous acid salts are very common with monocarboxylic acids.

Two fundamental types of acid salts are recognised: the first type has the two X units non-equivalent and characterisable as anion and neutral molecule, $M^+X^-.HX$, and are classified as type B[13]. The second type gives a more interesting situation in that the two X units of the formula are crystallographically equivalent; such structures are classified as type A.[13] The title structure can be represented as an acid salt of the type $BH^+.X^-.2HX$. For the physical chemist the main interest of these structures arises because many of them involve short H bonds. Type B acid salts give rise to non-symmetrical, non-equivalent H bonds while short symmetrical bonds seem to be the rule in the type A acid salts.

TABLE 1 : Some results of Hydrogen atom location by neutron diffraction methods.[9-10]

COMPOUND	H BOND	r(A-H) Å	r(A-B) Å	A-H-B(°)	CURVE
KH Maleate	O..H..O	1.22	2.44±0.02	180	ssm[a]
KHChloromaleate	O..H..O	1.22	2.403±0.003	175	ssm
$HCrO_2$	O..H..O	1.26	2.49±0.02	180	ssm
$DCrO_2$	O..H..O	0.96	2.55±0.02	180	ssm
D_2O (123K)	O-H..O	0.997	2.75±0.007	180	sdm[a]
KH_2PO_4 (298K)	O-H..O	1.085±0.013	2.487±0.005	180	sdm
KH_2PO_4 (77K)	O-H..O	1.05±0.014	2.486±0.004	180	-
N-acetylglycine	O-H..O	1.06±0.03	2.55±0.02	173	-

a : ssm = symmetrical single minimum potential energy curve,
sdm = symmetrical double minimum potential energy curve.

TABLE 2 : The location of hydrogen and deuterium atoms in the H bonds in crystalline hydrates found by neutron diffraction[9-11]

COMPOUND	r(O'-H) Å	r(O'-O") Å	O'-H-O" (°)
$NaHCO_3.Na_2CO_3.2H_2O$	1.25	2.50±0.02	180
Oxalic acid	1.057±0.02	2.518±0.01	175
$(COOH)_2.2H_2O$	0.968±0.03	2.856±0.01	156
	0.945±0.02	2.840±0.01	167
Oxalic acid	1.042±0.008	2.540±0.004	174.37±0.64
$(COOD)_2.2D_2O$	0.946±0.01	2.854±0.005	155.83±0.68
	0.960±0.01	2.822±0.004	169.10±0.84
$NiSO_4.6D_2O$	0.93	2.69	167
	0.97	2.74	167
	0.96	2.75	167
	0.97	2.77	154
	1.00	2.81	168
	0.96	2.84	154

5.2 EXPERIMENTAL

Cycloundec-1-ene carboxylic acid is available commercially as a white powdered material. A simple acid/base reaction between this and 1,8-bis(dimethylamino) naphthalene in a non-acidic or non-basic solvent such as methylene chloride resulted in the title structure.

Crystal Data.

Dimethyl (8'-dimethylaminonaphthyl)ammonium dihydrogen tris(cycloundec-1-ene carboxylate), $C_{50}H_{78}N_2O_6$, M = 803.20 amu, monoclinic, $\underline{a}$ = 14.047(9), $\underline{b}$ = 20.631(9), $\underline{c}$ = 17.955(2) Å, β = 112.80°, U = 4797.07 Å^3, D$\underline{c}$ = 1.11 g.cm.$^{-3}$, Z = 4, F(000) = 1760, μ(Mo-Kα) = 0.77 cm.$^{-1}$, Space Group = $P2_1/a$.

Data Collection.

Instrument used: Enraf-Nonius CAD4 diffractometer.
Radiation used: Mo-Kα, λ = 0.71069 Å.
Monochromation used: graphite crystal.
Upper limit for data collection: Θ_{max} = 26°.
Number of independent observed reflections: m = 3563.
Unobserved cut-off: $2.0\sigma_I$.
Number of parameters refined: n = 146.
Number of reflections per parameter: m/n = 24.4

Cell dimensions were derived from least-squares treatment of the setting angles for 25 reflections. For intensity measurements, 7648 reflections $\underline{hkl}$ and $\underline{hk\bar{l}}$ were surveyed in the range $\Theta \leqslant 26°$ and 3563 reflections satisfied the criterion, $I > 2.0\sigma_I$.

Standard reflections showed a significant variation towards the end of data collection and were used to place the measured intensities on a common scale.

Structure Analysis.

The crystal structure was solved using a modified version of MULTAN[14] which incorporates higher invariants[15]. 622 quartets were produced using QGEN for the top 100 E-magnitudes having $|E| \geqslant 2.5$ with $P^{\pm}_{7} \geqslant 0.6$ and $P^{\pm}_{13} \geqslant 0.7$.

Triplet phase relationships were generated for the top 340 E-magnitudes with $|E| \geqslant 1.20$. An E-map computed from the set with the lowest NQUEST[15] (-0.33) figure of merit revealed a 28 atom fragment. Weighted Fourier calculations based on this fragment solved for all non-hydrogen atoms. The approximate coordinates and anisotropic thermal parameters were refined by several cycles of full-matrix least-squares calculations via SHELX[16]. A difference synthesis at R = 0.103 revealed all the hydrogen atoms, which were subsequently included in further least-squares refinement. The hydrogen atom positional and isotropic thermal parameters were refined, except for the hydrogen atoms of ring C which were geometrically constrained but whose isotropic temperature factors were refined. A weighting scheme , $w = 1/\sigma^2 \underline{(F)}$ was adopted. These calculations reduced R to a final value of 0.0636 (R_w = 0.0665).

5.3 RESULTS

Final structure factors (observed and calculated) are included in the appendices.

TABLE 3a: Fractional atomic coordinates (x/a, y/b, z/c) ($x10^4$) with esd's in parentheses for the non-hydrogen atoms of the dimethyl (8'-dimethylaminonaphthyl) ring.

TABLE 4a: Fractional atomic coordinates ($x10^4$) with esd's in parentheses for the non-hydrogen atoms of ring A.

TABLE 5a: Fractional atomic coordinates ($x10^4$) with esd's in parentheses for the non-hydrogen atoms of ring B.

TABLE 6a: Fractional atomic coordinates ($x10^4$) with esd's in parentheses for the non-hydrogen atoms of ring C.

TABLE 3b: Fractional atomic coordinates ($x10^3$) and U isotropic ($x10^3$ Å^2) for the hydrogen atoms of the dimethyl (8'-dimethylaminonaphthyl) ring.

TABLE 4b: Fractional atomic coordinates ($x10^3$) and U isotropic ($x10^3$ Å^2) for hydrogen atoms of ring A.

TABLE 5b: Fractional atomic coordinates ($x10^3$) and U isotropic ($x10^3$ Å^2) for hydrogen atoms of ring B.

TABLE 6b: Fractional atomic coordinates ($x10^3$) and U isotropic ($x10^3$ Å^2) for hydrogen atoms of ring C.

TABLE 3c: Thermal parameters (U_{11}, U_{22}, U_{33}, U_{23}, U_{13}, U_{12}) ($x10^3$ Å^2) for non-hydrogen atoms of dimethyl (8'-dimethylaminonaphthyl) ring.

TABLE 4c: Thermal parameters (U_{11}, U_{22}, U_{33}, U_{23}, U_{13}, U_{12})

($x10^3$ Å^2) for non-hydrogen atoms of ring A.

TABLE 5c: Thermal parameters (U_{11}, U_{22}, U_{33}, U_{23}, U_{13}, U_{12}) ($x10^3$ Å^2) for non-hydrogen atoms of ring B.

TABLE 6c: Thermal parameters (U_{11}, U_{22}, U_{33}, U_{23}, U_{13}, U_{12}) ($x10^3$ Å^2) for non-hydrogen atoms of ring C.

TABLE 7: Bond lengths for ring structures (Å).

TABLE 8a: Valence angles (°) for dimethyl (8'-dimethylamino naphthyl) ring.

TABLE 8b: Valence angles (°) for ring A.

TABLE 8c: Valence angles (°) for ring B.

TABLE 8d: Valence angles (°) for ring C.

TABLE 9a: Torsion angles (°) for dimethyl (8'-dimethylaminonaphthyl) ring.

TABLE 9b: Torsion angles (°) for ring A.

TABLE 9c: Torsion angles (°) for ring B.

TABLE 9d: Torsion angles (°) for ring C.

Molecular representations of each of the four fragments were prepared by ORTEP[17] and are given in Figures 5.2 a-d. The crystal packing arrangement is viewed in Figure 5.3.

TABLE 3a

C(1)	3906(3)	8873(2)	5536(2)
C(2)	4280(4)	9184(2)	5039(3)
C(3)	3667(5)	9595(2)	4437(3)
C(4)	2674(5)	9689(2)	4328(3)
C(5)	1195(4)	9472(3)	4687(3)
C(6)	0791(4)	9181(3)	5170(4)
C(7)	1392(3)	8788(3)	5825(3)
C(8)	2415(3)	8687(2)	5963(2)
C(9)	2872(3)	8967(2)	5462(2)
C(10)	2223(3)	9372(2)	4816(2)
N(1)	3062(3)	8316(2)	6679(2)
C(11)	2724(5)	7639(3)	6688(5)
C(12)	3189(5)	8644(3)	7433(3)
N(2)	4546(2)	8418(1)	6144(2)
C(13)	5576(4)	8672(3)	6635(3)
C(14)	4631(5)	7796(3)	5769(4)

TABLE 4a

C(1A)	2664(3)	1649(3)	5942(3)
C(2A)	3189(5)	2173(3)	6302(4)
C(3A)	3785(11)	2646(4)	6025(6)
C(4A)	4904(13)	2638(8)	6554(8)
C(5A)	5486(10)	1909(11)	6670(11)
C(6A)	5461(7)	1512(8)	7419(5)
C(7A)	5423(11)	0810(9)	7336(9)
C(8A)	4434(11)	0577(5)	6798(6)
C(9A)	3703(10)	0598(4)	7197(5)
C(10A)	2647(10)	0573(4)	6584(7)
C(11A)	2189(6)	1202(6)	6372(4)
C(12A)	2540(4)	1469(2)	5113(3)
O(1A)	3193(3)	1502(2)	4833(2)
O(2A)	1605(3)	1254(2)	4696(2)

TABLE 5a

C(1B)	6853(3)	8021(2)	9175(3)
C(2B)	6750(4)	8637(3)	9322(3)
C(3B)	5908(4)	9103(3)	8900(3)
C(4B)	5329(5)	9360(3)	9403(4)
C(5B)	4898(5)	8819(4)	9766(4)
C(6B)	5640(7)	8642(4)	10626(4)
C(7B)	5533(6)	7961(5)	10890(4)
C(8B)	5891(4)	7466(4)	10466(4)
C(9B)	7049(5)	7371(4)	10797(4)
C(10B)	7466(5)	7894(3)	10183(4)
C(11B)	7759(4)	7616(3)	9698(4)
C(12B)	6071(4)	7673(2)	8466(3)
O(1B)	5166(3)	7783(2)	8188(2)
O(2B)	6483(3)	7216(2)	8182(2)

TABLE 6a

C(1C)	4844(5)	5983(2)	8151(3)
C(2C)	5681(5)	5723(3)	8595(3)
C(3C)	6546(4)	5500(4)	8384(4)
C(4C)	6777(8)	4822(5)	8527(9)
C(5C)	6099(11)	4329(4)	8119(8)
C(6C)	4848(19)	4147(10)	7938(11)
C(7C)	4962(15)	4188(6)	8642(7)
C(8C)	3617(11)	4360(7)	8184(12)
C(9C)	3338(7)	4919(6)	8383(10)
C(10C)	3410(9)	5522(7)	8477(10)
C(11C)	3915(6)	6134(3)	8422(4)
C(12C)	4627(5)	6149(2)	7275(3)
O(1C)	5237(3)	6520(2)	7120(2)
O(2C)	3836(3)	5917(2)	6764(2)

TABLE 3b

H(2)	497(4)	908(2)	511(3)	97(17)
H(3)	3961(34)	9870(22)	4051(28	114(16)
H(4)	228(3)	997(2)	395(2)	77(14)
H(5)	076(4)	981(2)	417(3)	126(17)
H(6)	0166(30)	9222(16)	5093(21)	56(12)
H(7)	117(2)	856(2)	617(2)	49(11)
H(11A)	204(4)	762(2)	677(2)	94(15)
H(11B)	3277(36)	7444(22)	7093(27)	104(19)
H(11C)	2593(36)	7452(22)	6211(28)	93(20)
H(12A)	2663(39)	8662(23)	7552(27)	93(19)
H(12B)	341(3)	906(2)	740(2)	80(15)
H(12C)	3645(34)	8365(20)	7919(27)	98(15)
H(13A)	5455(34)	9100(24)	6848(26)	102(17)
H(13B)	590(3)	872(2)	629(2)	70(13)
H(13C)	5861(27)	8336(18)	7049(22)	70(12)
H(14A)	487(3)	748(2)	619(2)	62(11)
H(14B)	498(4)	794(2)	535(3)	120(17)
H(14C)	3870(36)	7652(20)	5420(25)	99(16)
H′	362(3)	830(2)	660(2)	83(15)

TABLE 4b

H(2)	311(4)	225(3)	674(3)	121(23)
H(3A)	3755(48)	2533(29)	5486(41)	155(26)
H(3B)	341(5)	310(3)	607(4)	177(27)
H(4A)	525(12)	266(7)	629(9)	273(78)
H(4B)	5489(45)	2428(31)	7102(36)	130(21)
H(5A)	618(4)	174(2)	694(3)	110(19)
H(5B)	517(7)	169(5)	620(6)	235(52)
H(6A)	4880(53)	1704(29)	7528(35)	153(26)
H(6B)	603(7)	154(4)	772(6)	182(43)
H(7A)	551(8)	066(5)	810(7)	293(50)
H(7B)	5698(84)	0479(56)	7035(65)	276(59)
H(8A)	423(4)	081(3)	618(4)	139(20)
H(8B)	443(7)	012(4)	671(5)	228(41)
H(9A)	4023(52)	0281(34)	7675(44)	193(28)
H(9B)	395(4)	106(3)	766(3)	130(17)
H(10A)	237(8)	024(5)	710(7)	352(49)
H(10B)	2527(39)	0356(25)	6055(35)	129(20)
H(11A)	153(5)	117(3)	610(4)	168(29)
H(11B)	230(4)	147(2)	686(3)	113(17)
H(O)	1439(43)	1179(27)	4086(37)	159(23)

TABLE 5b

H(2)	728(3)	878(2)	975(2)	60(13)
H(3A)	622(3)	946(2)	874(2)	71(13)
H(3B)	5355(35)	8872(21)	8380(28)	100(15)
H(4A)	4727(39)	9714(25)	9063(29)	130(19)
H(4B)	5856(33)	9637(22)	9867(27)	101(16)
H(5A)	436(4)	897(3)	985(3)	123(22)
H(5B)	4731(30)	8455(19)	8406(25)	80(14)
H(6A)	5663(40)	9006(28)	11055(36)	146(21)
H(6B)	629(5)	869(3)	1064(4)	141(30)
H(7A)	5965(40)	8054(24)	11524(35)	137(19)
H(7B)	468(6)	811(3)	1082(4)	193(25)
H(8A)	555(3)	700(2)	1046(2)	107(16)
H(8B)	5568(34)	7610(21)	9796(29)	115(15)
H(9A)	742(4)	790(2)	1096(3)	121(17)
H(9B)	715(3)	707(2)	1127(3)	106(15)
H(10A)	7065(51)	6733(31)	9757(39	174(29)
H(10B)	804(4)	679(2)	1042(3)	111(17)
H(11A)	806(3)	736(2)	931(2)	81(13)
H(11B)	8244(35)	7939(22)	10049(26)	99(16)
H(O)	596(4)	700(3)	774(3)	146(24)

TABLE 6b

H(2)	578(0)	565(0)	922(0)	148(20)
H(3A)	7227(4)	5773(4)	8739(4)	294(46)
H(3B)	635(0)	559(0)	775(0)	230(32)
H(4A)	694(1)	475(1)	916(1)	350(75)
H(4B)	7470(8)	4743(5)	8416(9)	196(27)
H(5A)	610(1)	436(0)	752(1)	558(70)
H(5B)	651(1)	390(0)	841(1)	332(50)
H(6A)	4628(19)	3667(10)	7692(11)	275(44)
H(6B)	431(2)	450(1)	755(1)	221(39)
H(7A)	517(2)	375(1)	899(1)	664(69)
H(7B)	5447(15)	4580(6)	8980(7)	205(32)
H(8A)	321(1)	398(1)	836(1)	552(70)
H(8B)	339(1)	435(1)	754(1)	546(69)
H(9A)	3332(7)	4779(6)	8961(10)	469(70)
H(9B)	256(1)	492(1)	793(1)	515(71)
H(10A)	261(1)	566(1)	818(1)	121(15)
H(10B)	3620(9)	5523(7)	9123(10)	118(20)
H(11A)	3353(6)	6436(3)	7975(4)	556(68)
H(11B)	4205(6)	6382(3)	8997(4)	396(66)

TABLE 3c

C(1)	62(3)	46(2)	56(2)	-1(2)	26(2)	3(2)
C(2)	77(3)	70(3)	72(3)	17(2)	37(3)	9(3)
C(3)	103(4)	84(4)	79(3)	20(3)	44(3)	14(3)
C(4)	122(5)	66(3)	53(3)	15(2)	20(3)	24(3)
C(5)	75(4)	87(4)	79(3)	-5(3)	17(3)	15(3)
C(6)	38(3)	105(4)	113(5)	-21(4)	10(3)	17(3)
C(7)	51(3)	86(4)	87(4)	-4(3)	26(3)	-2(3)
C(8)	46(3)	56(2)	69(3)	-7(2)	19(2)	1(2)
C(9)	49(2)	51(2)	54(2)	-6(2)	20(2)	1(2)
C(10)	65(3)	59(3)	55(3)	-4(2)	12(2)	17(2)
N(1)	43(2)	56(2)	66(2)	2(2)	29(2)	2(2)
C(11)	83(4)	65(4)	104(5)	2(4)	40(4)	-8(3)
C(12)	66(3)	92(4)	72(4)	-5(3)	30(3)	9(3)
N(2)	46(2)	55(2)	60(2)	8(2)	23(2)	8(2)
C(13)	61(3)	100(4)	73(3)	15(3)	27(3)	7(3)
C(14)	9 (4)	67(3)	93(4)	17(3)	42(4)	21(3)

TABLE 4c

C(1A)	57(3)	90(3)	63(3)	-8(3)	13(2)	8(3)
C(2A)	125(5)	106(5)	76(4)	-6(4)	20(4)	33(4)
C(3A)	322(15)	70(5)	127(7)	12(4)	84(9)	-48(7)
C(4A)	227(13)	262(15)	140(8)	-8(9)	34(10)	-171(13)
C(5A)	132(9)	351(24)	203(15)	-94(18)	107(10)	-82(13)
C(6A)	83(6)	329(18)	91(6)	-58(8)	2(5)	-12(8)
C(7A)	202(12)	281(17)	161(11)	-59(11)	14(9)	90(12)
C(8A)	237(12)	163(8)	97(6)	-11(6)	38(7)	110(8)
C(9A)	251(11)	115(6)	65(4)	11(4)	26(6)	-33(7)
C(10A)	254(12)	108(6)	123(8)	-19(6)	96(9)	-52(7)
C(11A)	93(5)	228(10)	68(4)	-41(6)	39(4)	-51(6)
C(12A)	66(3)	75(3)	58(3)	-2(2)	10(3)	7(3)
O(1A)	109(3)	142(3)	74(2)	-4(2)	44(2)	-18(2)
O(2A)	86(2)	113(3)	59(2)	-10(2)	14(2)	2(2)

TABLE 5c

C(1B)	57(3)	76(3)	69(3)	7(3)	28(2)	2(3)
C(2B)	67(3)	86(4)	74(3)	-7(3)	32(3)	-17(3)
C(3B)	9[illegible](4)	71(3)	96(4)	6(3)	42(3)	-2(3)
C(4B)	11[illegible](4)	88(4)	101(4)	-12(4)	55(4)	12(4)
C(5B)	84(4)	130(6)	85(4)	-12(4)	40(3)	8(4)
C(6B)	159(7)	134(6)	83(4)	-23(4)	56(5)	-40(5)
C(7B)	123(6)	212(9)	75(4)	-10(5)	43(4)	8(6)
C(8B)	73(4)	141(6)	98(4)	34(4)	20(3)	-13(4)
C(9B)	96(5)	161(6)	84(4)	42(4)	22(4)	7(4)
C(10B)	83(4)	113(5)	105(5)	32(4)	18(4)	28(4)
C(11B)	61(3)	99(4)	95(4)	0(4)	21(3)	5(3)
C(12B)	7[illegible](3)	72(3)	65(3)	4(2)	32(3)	7(3)
O(1B)	66(2)	106(2)	100(2)	-27(2)	11(2)	16(2)
O(2B)	8 (2)	85(2)	91(2)	-12(2)	41(2)	7(2)

TABLE 6c

C(1C)	125(5)	73(3)	67(3)	0(3)	17(3)	-5(3)
C(2C)	97(4)	102(4)	84(4)	9(3)	16(3)	-24(3)
C(3C)	62(4)	180(7)	161(6)	105(5)	39(4)	26(4)
C(4C)	170(9)	185(10)	317(15)	62(10)	158(9)	86(8)
C(5C)	307(15)	91(6)	279(13)	59(7)	193(12)	57(8)
C(6C)	344(23)	429(26)	310(21)	-215(20)	29(20)	70(23)
C(7C)	510(29)	158(9)	164(9)	100(8)	-14(14)	-83(14)
C(8C)	254(15)	208(13)	301(17)	-8(13)	19(14)	-21(12)
C(9C)	111(7)	205(12)	397(18)	57(13)	57(9)	-67(8)
C(10C)	395(20)	322(20)	735(36)	12(21)	509(25)	68(15)
C(11C)	155(6)	129(5)	121(5)	1(4)	87(4)	38(4)
C(12C)	127(4)	50(3)	50(3)	-2(2)	16(3)	2(3)
O(1C)	112(2)	69(2)	61(2)	2(2)	31(2)	-5(2)
O(2C)	155(3)	106(3)	56(2)	0(2)	3(2)	-50(2)

TABLE 7

C(1) - C(2)	1·359(6)	C(12A)- O(1A)	1·208(6)
C(1) - C(9)	1·419(5)	C(12A)- O(2A)	1·311(6)
C(1) - N(2)	1·456(5)	C(1B) - C(2B)	1·318(7)
C(2) - C(3)	1·388(7)	C(1B) - C(11B)	1·507(7)
C(3) - C(4)	1·346(9)	C(1B) - C(12B)	1·503(6)
C(4) - C(10)	1·424(7)	C(2B) - C(3B)	1·484(8)
C(5) - C(6)	1·348(8)	C(3B) - C(4B)	1·525(9)
C(5) - C(10)	1·386(7)	C(4B) - C(5B)	1·531(9)
C(6) - C(7)	1·408(8)	C(5B) - C(6B)	1·536(9)
C(7) - C(8)	1·376(6)	C(6B) - C(7B)	1·509(13)
C(8) - C(9)	1·415(5)	C(7B) - C(8B)	1·473(11)
C(8) - N(1)	1·469(5)	C(8B) - C(9B)	1·513(8)
C(9) - C(10)	1·434(5)	C(9B) - C(10B)	1·544(9)
N(1) - C(11)	1·477(6)	C(10B)- C(11B)	1·538(9)
N(1) - C(12)	1·461(6)	C(12B)- O(1B)	1·194(6)
N(2) - C(13)	1·469(6)	C(12B)- O(2B)	1·309(6)
N(2) - C(14)	1·474(6)	C(1C) - C(2C)	1·257(8)
C(1A) - C(2A)	1·328(8)	C(1C) - C(11C)	1·590(9)
C(1A) - C(11A)	1·513(10)	C(1C) - C(12C)	1·521(6)
C(1A) - C(12A)	1·477(6)	C(2C) - C(3C)	1·479(8)
C(2A) - C(3A)	1·490(13)	C(3C) - C(4C)	1·436(13)
C(3A) - C(4A)	1·49(2)	C(4C) - C(5C)	1·392(16)
C(4A) - C(5A)	1·69(3)	C(5C) - C(6C)	1·70(3)
C(5A) - C(6A)	1·59(2)	C(6C) - C(7C)	1·21(2)
C(6A) - C(7A)	1·45(3)	C(7C) - C(8C)	1·78(2)
C(7A) - C(8A)	1·43(2)	C(8C) - C(9C)	1·31(2)
C(8A) - C(9A)	1·463(17)	C(9C) - C(10C)	1·255(19)
C(9A) - C(10A)	1·466(17)	C(10C)- C(11C)	1·478(15)
C(10A)- C(11A)	1·433(15)	C(12C)- O(1C)	1·258(6)
		C(12C)- O(2C)	1·231(6)

TABLE 8a

C(9)	C(1)	C(2)	121.1(4)	N(2)	C(1)	C(2)	120.9(4)
C(3)	C(2)	C(1)	121.4(5)	N(2)	C(1)	C(9)	118.0(3)
C(8)	C(9)	C(1)	125.8(3)	C(10)	C(9)	C(1)	117.5(3)
C(13)	N(2)	C(1)	113.4(3)	C(14)	N(2)	C(1)	110.8(3)
C(4)	C(3)	C(2)	120.3(5)	C(10)	C(4)	C(3)	121.8(5)
C(5)	C(10)	C(4)	120.8(4)	C(9)	C(10)	C(4)	118.1(4)
C(10)	C(5)	C(6)	119.8(5)	C(7)	C(6)	C(5)	121.9(5)
C(9)	C(10)	C(5)	121.1(4)	C(8)	C(7)	C(6)	118.9(4)
C(9)	C(8)	C(7)	121.6(4)	N(1)	C(8)	C(7)	119.0(4)
N(1)	C(8)	C(9)	119.3(3)	C(10)	C(9)	C(8)	116.7(3)
C(11)	N(1)	C(8)	114.2(4)	C(12)	N(1)	C(8)	112.4(4)
C(12)	N(1)	C(11)	110.5(4)	C(14)	N(2)	C(13)	110.5(4)

TABLE 8b

C(11A)- C(1A) - C(2A)	121.4(5)	C(12A)- C(1A) - C(2A)	121.4(5)
C(3A) - C(2A) - C(1A)	130.5(7)	C(12A)- C(1A) - C(11A)	117.2(5)
C(10A)- C(11A)- C(1A)	116.5(7)	O(1A) - C(12A)- C(1A)	126.4(4)
O(2A) - C(12A)- C(1A)	111.2(4)	C(4A) - C(3A) - C(2A)	111.8(9)
C(5A) - C(4A) - C(3A)	115.5(12)	C(6A) - C(5A) - C(4A)	113.3(12)
C(7A) - C(6A) - C(5A)	116.0(12)	C(8A) - C(7A) - C(6A)	113.0(12)
C(9A) - C(8A) - C(7A)	109.9(10)	C(10A)- C(9A) - C(8A)	109.2(8)
C(11A)- C(10A)- C(9A)	112.7(8)	O(2A) - C(12A)- O(1A)	122.4(4)

TABLE 8c

C(11B)- C(1B) - C(2B)	122.8(4)	C(12B)- C(1B) - C(2B)	122.0(4)
C(3B) - C(2B) - C(1B)	130.6(5)	C(12B)- C(1B) - C(11B)	115.2(4)
C(10B)- C(11B)- C(1B)	113.2(4)	O(1B) - C(12B)- C(1B)	124.9(4)
O(2B) - C(12B)- C(1B)	112.7(4)	C(4B) - C(3B) - C(2B)	115.1(5)
C(5B) - C(4B) - C(3B)	112.9(5)	C(6B) - C(5B) - C(4B)	112.1(6)
C(7B) - C(6B) - C(5B)	115.2(6)	C(8B) - C(7B) - C(6B)	112.9(6)
C(9B) - C(8B) - C(7B)	114.7(6)	C(10B)- C(9B) - C(8B)	114.5(5)
C(11B)- C(10B)- C(9B)	113.9(6)	O(2B) - C(12B)- O(1B)	122.3(4)

TABLE 8d

C(11C)- C(1C) - C(2C)	124.5(5)	C(12C)- C(1C) - C(2C)	121.0(5)
C(3C) - C(2C) - C(1C)	129.1(6)	C(12C)- C(1C) - C(11C)	114.4(5)
C(1C)- C(11C)- C(1C)	109.2(7)	O(1C) - C(12C)- C(1C)	119.0(4)
O(2C) - C(12C)- C(1C)	116.4(5)	C(4C) - C(3C) - C(2C)	114.1(6)
C(5C) - C(4C) - C(3C)	123.9(10)	C(6C) - C(5C) - C(4C)	134.9(12)
C(7C) - C(6C) - C(5C)	94.4(16)	C(8C) - C(7C) - C(6C)	81.1(15)
C(9C) - C(8C) - C(7C)	115.2(13)	C(10C)- C(9C) - C(8C)	153.1(13)
C(11C)- C(10C)- C(9C)	149.1(12)	O(2C) - C(12C)- O(1C)	124.6(4)

TABLE 9a

C(9)	C(1)	C(2)	C(3)	-0.9(7)	N(2)	C(1)	C(2)	C(3)	177.2(4)
C(2)	C(1)	C(9)	C(8)	-177.6(4)	C(2)	C(1)	C(9)	C(10)	3.5(6)
N(2)	C(1)	C(9)	C(8)	4.2(5)	N(2)	C(1)	C(9)	C(10)	-174.7(3)
C(2)	C(1)	N(2)	C(12)	48.6(5)	C(2)	C(1)	N(2)	C(14)	-76.2(5)
C(9)	C(1)	N(2)	C(14)	-133.2(4)	C(9)	C(1)	N(2)	C(14)	102.0(4)
C(1)	C(2)	C(3)	C(4)	-0.7(8)	C(2)	C(3)	C(4)	C(10)	-3.3(8)
C(3)	C(4)	C(10)	C(5)	-179.4(5)	C(3)	C(4)	C(10)	C(9)	2.9(7)
C(10)	C(5)	C(6)	C(7)	1.9(8)	C(6)	C(5)	C(10)	C(4)	-178.2(5)
C(6)	C(5)	C(10)	C(9)	-0.6(7)	C(5)	C(6)	C(7)	C(8)	-1.6(8)
C(6)	C(7)	C(8)	C(9)	-0.1(7)	C(6)	C(7)	C(8)	N(1)	175.7(4)
C(7)	C(8)	C(9)	C(1)	-177.6(4)	C(7)	C(8)	C(9)	C(10)	1.4(6)
N(1)	C(8)	C(9)	C(1)	6.6(6)	N(1)	C(8)	C(9)	C(10)	-174.5(3)
C(7)	C(8)	N(1)	C(11)	62.2(5)	C(7)	C(8)	N(1)	C(12)	-64.7(5)
C(9)	C(8)	N(1)	C(11)	-121.8(4)	C(9)	C(8)	N(1)	C(12)	111.2(4)
C(1)	C(9)	C(10)	C(4)	-4.4(6)	C(1)	C(9)	C(10)	C(5)	178.0(4)
C(8)	C(9)	C(10)	C(4)	176.6(4)	C(8)	C(9)	C(10)	C(5)	-1.8(6)

TABLE 9b

C(11A)- C(1A) - C(2A) - C(3A)	174.5(8)	C(12A)- C(1A) - C(2A) - C(3A)	-4.1(11)
C(2A) - C(1A) - C(11A)- C(10A)	-110.6(9)	C(12A)- C(1A) - C(11A)- C(10A)	68.3(9)
C(2A) - C(1A) - C(12A)- O(1A)	40.6(8)	C(2A) - C(1A) - C(12A)- O(2A)	-140.0(5)
C(11A)- C(1A) - C(12A)- O(1A)	-138.1(6)	C(11A)- C(1A) - C(12A)- O(2A)	41.4(7)
C(1A) - C(2A) - C(3A) - C(4A)	-116.1(11)	C(2A) - C(3A) - C(4A) - C(5A)	55.4(15)
C(3A) - C(4A) - C(5A) - C(6A)	-90.8(16)	C(4A) - C(5A) - C(6A) - C(7A)	148.7(13)
C(5A) - C(6A) - C(7A) - C(8A)	-73.4(17)	C(6A) - C(7A) - C(8A) - C(9A)	-76.1(14)
C(7A) - C(8A) - C(9A) - C(10A)	161.2(11)	C(8A) - C(9A) - C(10A)- C(11A)	-96.5(11)
C(9A) - C(10A)- C(11A)- C(1A)	66.5(11)		

TABLE 9c

C(11B)- C(1B) - C(2B) - C(3B)	-177.7(5)		
C(12B)- C(1B) - C(2B) - C(3B)	2.7(8)	C(2B) - C(1B) - C(11B)- C(10B)	110.8(6)
C(12B)- C(1B) - C(11B)- C(10B)	-69.6(6)	C(2B) - C(1B) - C(12B)- O(1B)	-32.7(7)
C(2B) - C(1B) - C(12B)- O(2B)	148.6(5)	C(11B)- C(1B) - C(12B)- O(1B)	147.8(5)
C(11B)- C(1B) - C(12B)- O(2B)	-30.9(6)	C(1B) - C(2B) - C(3B) - C(4B)	110.1(6)
C(2B) - C(3B) - C(4B) - C(5B)	-54.3(7)	C(3B) - C(4B) - C(5B) - C(6B)	93.8(7)
C(4B) - C(5B) - C(6B) - C(7B)	-154.5(6)	C(5B) - C(6B) - C(7B) - C(8B)	70.0(9)
C(6B) - C(7B) - C(8B) - C(9B)	80.3(8)	C(7B) - C(8B) - C(9B) - C(10B)	-155.3(6)
C(8B) - C(9B) - C(10B)- C(11B)	90.2(7)	C(9B) - C(10B)- C(11B)- C(1B)	-63.0(7)

TABLE 9d

C(11C)- C(1C) - C(2C) - C(3C)	173.8(6)	C(12C)- C(1C) - C(2C) - C(3C)	-3.7(1)
C(2C) - C(1C) - C(11C)- C(1 C)	-72.2(9)	C(12C)- C(1C) - C(11C)- C(1 C)	104.7(8)
C(2C) - C(1C) - C(12C)- O(1C)	-57.8(7)	C(2C) - C(1C) - C(12C)- O(2C)	124. (6)
C(11C)- C(1C) - C(12C)- O(1C)	125.2(5)	C(11C)- C(1C) - C(12C)- O(2C)	-55.1(6)
C(1C) - C(2C) - C(3C) - C(4C)	-120.9(8)	C(2C) - C(3C) - C(4C) - C(5C)	64.5(13)
C(3C) - C(4C) - C(5C) - C(6C)	-52.4(21)	C(4C) - C(5C) - C(6C) - C(7C)	-51.4(23)
C(5C) - C(6C) - C(7C) - C(8C)	154.6(12)	C(6C) - C(7C) - C(8C) - C(9C)	-122.2(17)
C(7C) - C(8C) - C(9C) - C(1 C)	5 .5(37)	C(8C) - C(9C) - C(10C)- C(11C)	1.0(52)
C(9C) - C(1 C)- C(11C)- C(1C)	-4. (28)		

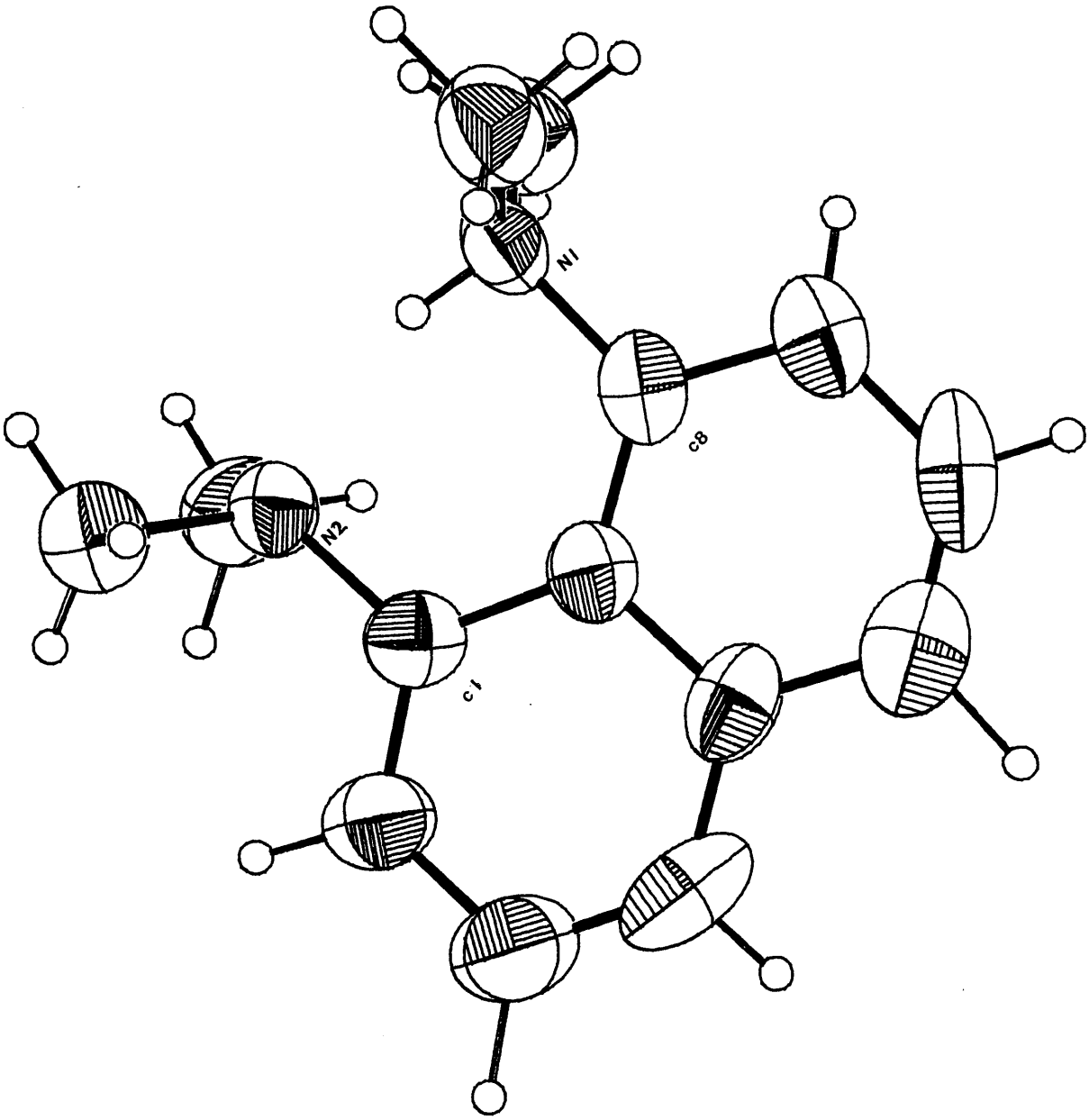


FIG.5.2a

naphthyl ring

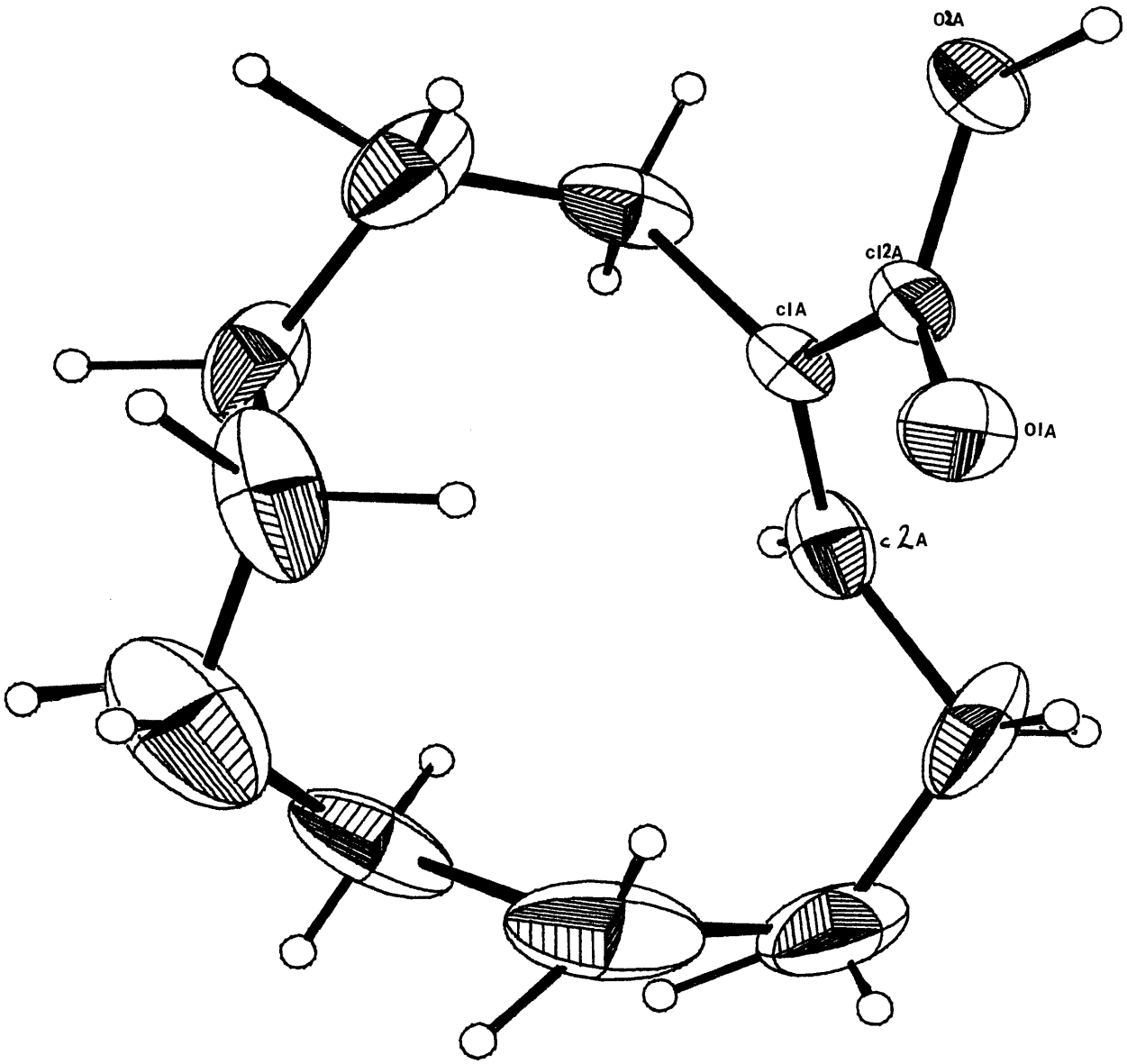
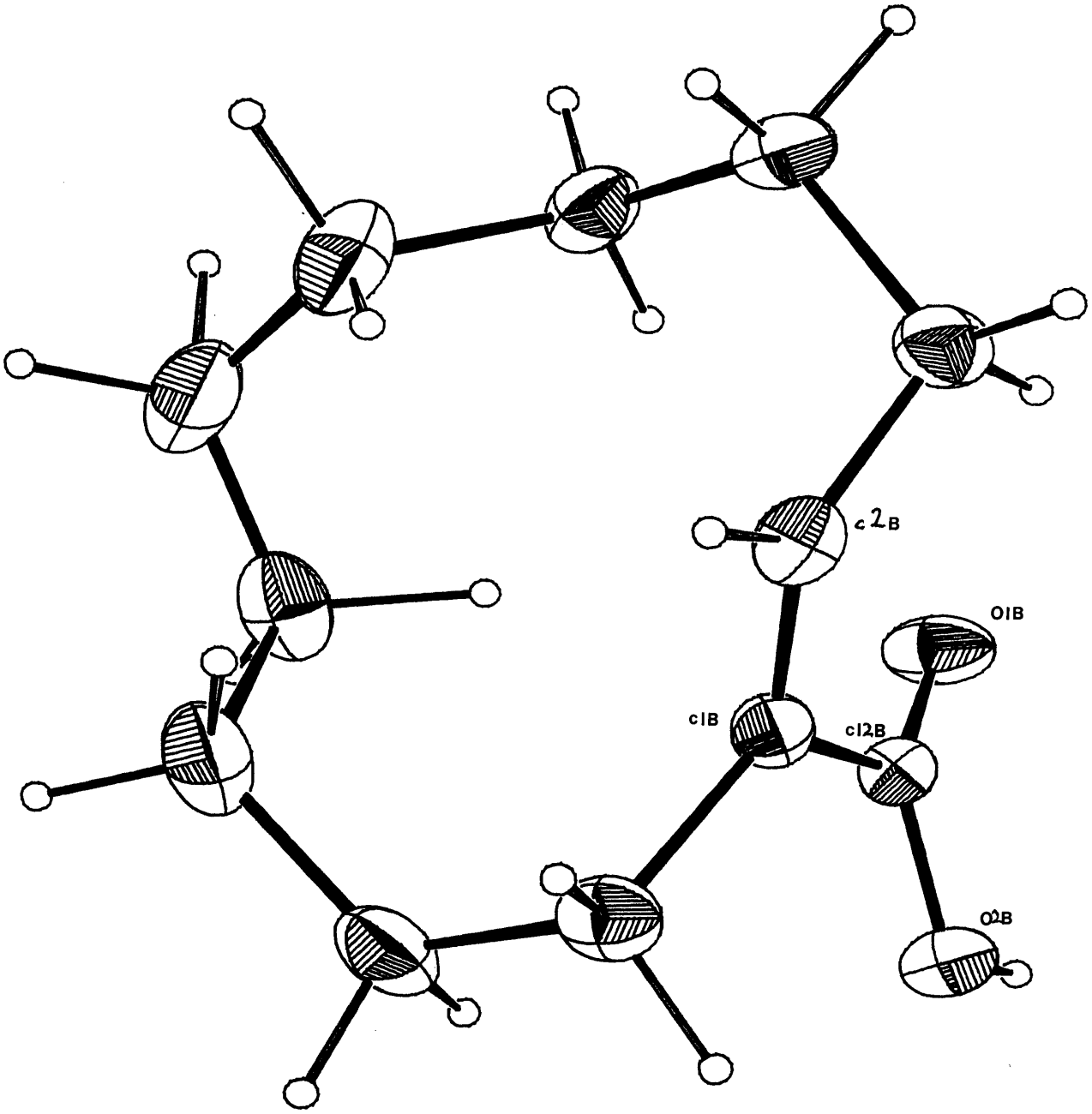


FIG. 52b

ring A

FIG. 52c

ring B



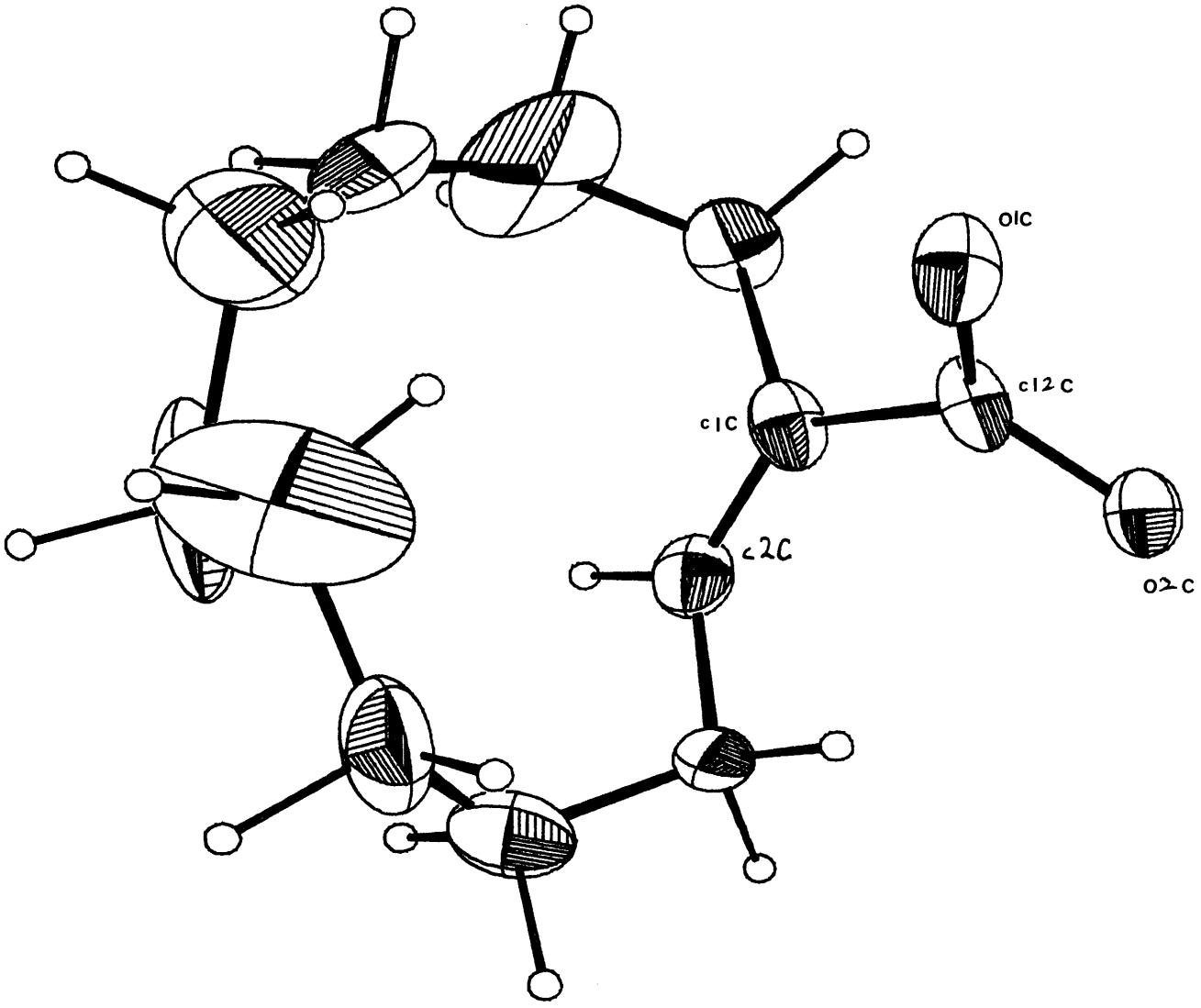


FIG. 5.2d

ring C

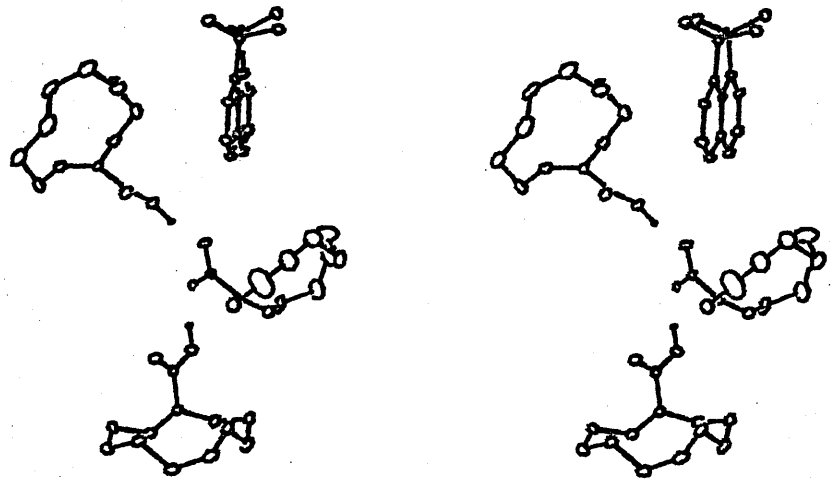


FIG. 5.3

5.4 DISCUSSION OF THE NAPHTHALENE RING

The remarkable basicity of 1,8-bis(dimethylamino)naphthalene has been examined by R.W.Alder[18] and coworkers whose recorded experimental pKa values (see Table 10) indicate that this compound is a stronger base than normal aliphatic amines! For this reason it has often been referred to as the "proton sponge".

TABLE 10

COMPOUND	R_1	R_2	pKa (in H_2O)
I	NH_2	NH_2	4.61
II	NHMe	NHMe	5.61
III	NMe_2	NHMe	6.43
IV	NMe_2	NMe_2	12.34

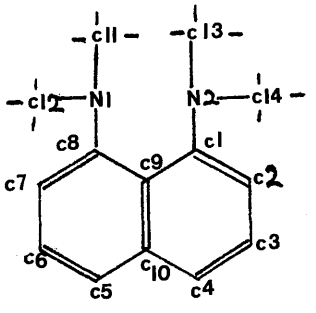
It seems (from a comparison of compounds III and IV) that introduction of an extra methyl group has greatly increased the basicity which in turn suggests, that compound IV is a highly strained molecule whose steric strains are relieved by protonation. Various crystal structure analyses of naphthalene and its derivatives have now been reported.[19-23] D.Bright[19] and his fellow researchers presented a crystal-structure analysis and strain-energy minimisation calculations on 1,8-dimethylnaphthalene. Their calculations do, indeed, suggest a strained molecule in the region of its substituents and they suggest that the repulsive energy between the methyl groups is decreased mainly by bond angle distortion at the junction between the methyl groups and the naphthalene nucleus. The inner angles at this junction are increased from their ideal unstrained values of 120° to an average value of 125° while there is a corresponding decrease in the outer angles to an average value of 116°.

The strain imposed on a naphthalene ring by introduction of

bulkier substituents on the 1,8 positions, must be considerably greater. H.Einspahr[20] and coworkers have produced corroboratory evidence for such a conclusion in their x-ray study of the structure of 1,8-bis(dimethylamino)naphthalene.

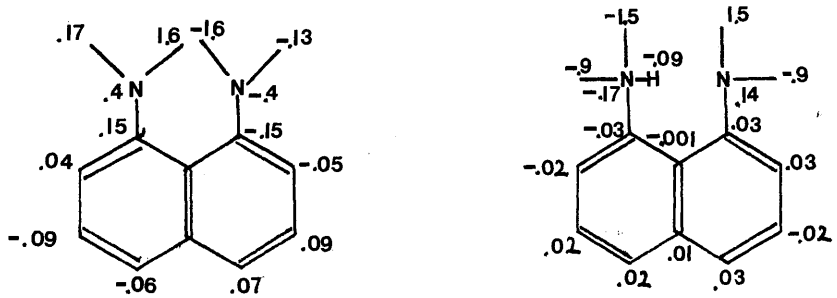
They find that the molecule adopts a conformation in which one carbon atom of each of the dimethylamino groups is eclipsed with respect to the naphthalene ring. Steric hindrance between the dimethylamino groups and/or resonance interactions between the dimethylamino groups and the aromatic ring are sufficiently great to distort the ring in several ways: one effect is a sizeable increase in the non-bonded $C_1....C_8$ distance (2.56 Å) compared to a non-bonded $C_4....C_5$ distance of 2.44 Å. (For an explanation of the numbering system involved see Figure 5.4). Another effect is a considerable twisting of the naphthalene ring into a non-planar conformation. Normally a strong resonance interaction between a dimethylamino group and an aromatic ring would favour a planar conformation but because of steric difficulties in this compound there is no reasonable possibility of bringing either of the dimethylamino groups into the plane of the naphthalene ring. Mean plane

FIG. 5.4: 1,8-bis(dimethylamino) naphthalene.



calculations demonstrate these distortions (see Figure 5.5). Repulsive energy between the substituents is decreased by bond-angle expansion for the C_8-C_9-C_1 angle to a value of 125.8° similar to that reported for 1,8-dimethylnaphthalene[19]. Close contact of one of the methyl groups on each nitrogen with ring hydrogens on C_7 and C_2 presumably prevents further expansion of the internal angles at the junction.

FIG. 5.5 : Mean plane calculations for the unprotonated[20] and protonated forms (title structure) of 1,8-bis(dimethylamino)naphthalene.



unprotonated

protonated

The astonishing basicity of 1,8-bis(dimethylamino)naphthalene suggests that the cation formed on protonation should be stable and that this cation is less sterically strained than its unprotonated form. Inspection of the crystal structure of the monoprotonated 1,8-bis(dimethylamino)naphthalene ring of the title structure

confirms the reduction in strain. The proton lies in the plane of the naphthalene ring between the two nitrogens, which are displaced on opposite sides of the plane of the ring. The non-bonded distance between atoms C_1 and C_8 is 2.52 Å which is less than the corresponding distance in the unprotonated form. The $C_4 \cdots C_5$ distance is the same as that recorded for both the unprotonated form and for 1,8-dimethylnaphthalene[23]. Mean plane calculations for the unprotonated[20] and protonated forms are recorded in Figure 5.5. The naphthalene ring in the protonated form is more nearly planar than the unprotonated form and, hence, suffers less steric difficulty. The nitrogens are displaced less from the mean plane in the cation than in the neutral form and one of the methyl groups on each of the nitrogens has moved from an eclipsed position with respect to the naphthalene ring to a gauche form, while the other moves from a trans form to a gauche form. Repulsion between the 1,8-substituents is decreased, once again, by expansion of the C_8-C_9-C_1 angle to a value of 125.8°.

In conjugated compounds there are considerable deviations from normal carbon-carbon single bond lengths (ca. 1.54 Å) and carbon=carbon double bond lengths (ca. 1.34 Å). With benzene, the bonds do not alternate in length as would be required for the Kekule formula but are all equivalent and of length 1.39 Å. With naphthalene, some bond length variation occurs, the shortest bonds being those which are calculated to have the largest bond orders[24-25]: the 1-2 bond[26] is significantly shorter than the 2-3, the 1-9 and the 9-10 bonds are, and also significantly shorter than the benzene bond lengths. (The 1-2 bond also refers to the 3-4, the 5-6 and the 7-8 bonds). This has been reproduced in all the crystal structures of naphthalene derivatives mentioned so far[19-23].

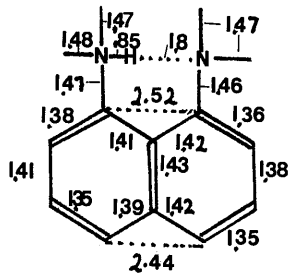
Crystal structures for monoprotonated 1,8-bis(dimethylamino)naphthalene have been reported[22] for isomorphous salts of Cu^{II} and Mg^{II} and results are in agreement with those reported here. Figure 5.6 indicates the calculated

bond lengths, Figure 5.7 the calculated valence angles and Figure 5.8, the mean plane calculations for these three structures.

In all three cases the proton lies in the plane of the naphthalene ring between the two nitrogens which are displaced above and below this plane. The proton appears closer to one nitrogen than to the other and it is displaced slightly from the plane to the same side as the nitrogen to which it is nearer.

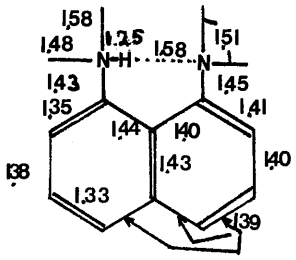
Comparison of the carbon-nitrogen bond lengths and C-N-C angles for the protonated and unprotonated form[20] of 1,8-bis(dimethylamino)naphthalene reveals some differences as expected. (See Figure 5.9). The protonated form has longer C-N distances and smaller C-N-C bond angles, indicative of tetrahedral geometry arrangements around each N.

The N....N non-bonded distance in the title structure is 2.619 Å which is considered a short hydrogen bond. Various theoretical calculations have been undertaken to study the hydrogen bond in the $[H_3N\text{-}H....NH_3]^+$ system[27-29]. The salient features of the work done by Tan and Linnett[27] are that firstly, there is contraction in the N....N separation in the symmetrical transition state for proton transfer, compared withthe N....N separation in the system of minimum energy i.e. the H-bonded complex, and that secondly, there is a low energy barrier for the proton transfer and a fairly strong H bond. Delpeuch and Serratrice[28] supported this general picture and predicted a double well potential for an N....N separation of 2.627 Å. They calculated that the minima of this double well occurred when the proton is displaced $\pm$0.5 Å from the mid-point of the N....N axis i.e. the distance of the proton from the nitrogens being ca. 0.8 and 1.8 Å. Merlet[29] and coworkers indicate that the nature of the potential energy diagrams obtained depends on the basis sets employed in the calculations but agree qualitatively with the aforementioned features and suggest that at relatively small



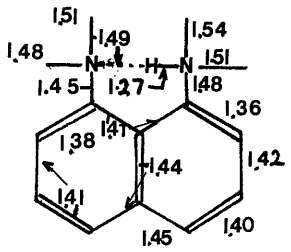
title study

N·····N 2.62



Mg^{II} salt[22]

N·····N 2.60

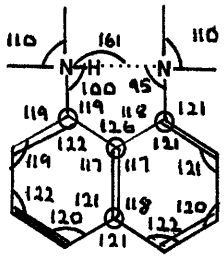


Cu^{II} salt[22]

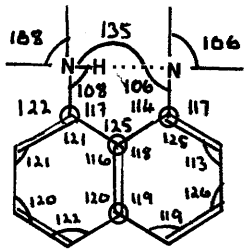
N·····N 2.65

FIG. 5.6

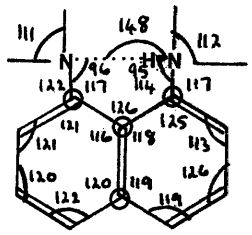
Bond lengths(Å) for protonated species



title study



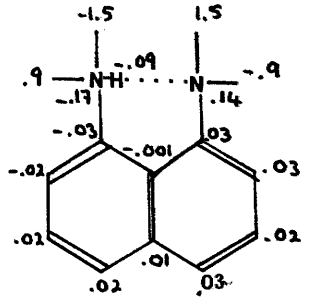
Mg^{II} salt[22]



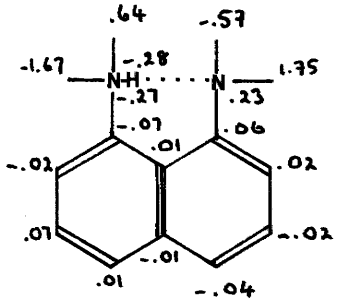
Cu^{II} salt[22]

FIG. 57

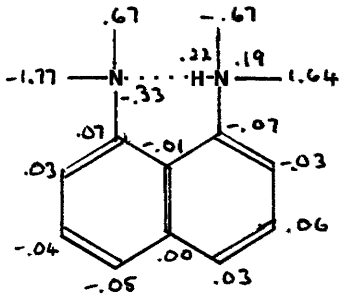
Bond angles (°) for protonated species



title study



Mg^{II} salt 22

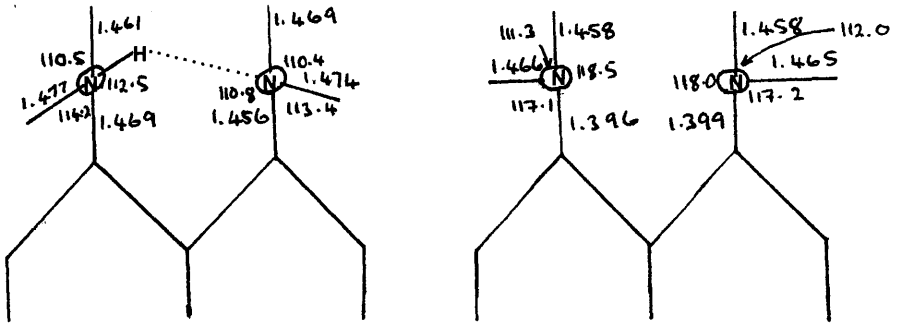


Cu^{II} salt 22

FIG. 5.8

Mean plane through atoms $C_1 - C_8$ inclusive.

values of N....N there is no double minimum potential, while at N....N of ca. 2.4 Å the situation changes rather suddenly as the double well potential begins to form. At an N....N distance of 2.60 Å they predict the minimum of energy to occur when the proton is 1.1 and 1.5 Å from the nitrogens, while the maximum of the double well occurs when the proton is at the mid-point of the N....N separation. No quantitative correlation can be made for the monoprotonated 1,8-bis(dimethylamino)naphthalene system from these theoretical calculations yet they can suggest that displacement of the hydrogen from the mid-point of the N....N distance is not totally unexpected.



title study reference 20

FIG. 5.9 Bond lengths in (Å).
Bond angles in (°).

5.5 DISCUSSION OF THE ACID SALT

Salts containing an unorthodoxly high proportion of acid have been known for at least 150 years and could, in the elementary context, be regarded as "super-acid" salts. The compound reported here falls into this class and is exactly analogous to sodium dihydrogen triacetate[30].

Discrete HX molecules and the X^- ion can be characterised in the salt from two pieces of information:
(a) The C-O distances and the C-C-O angles unambiguously distinguish the ionised and non-ionised carboxyl groups.
(b) The hydroxylic H atoms are located directly in a difference synthesis.

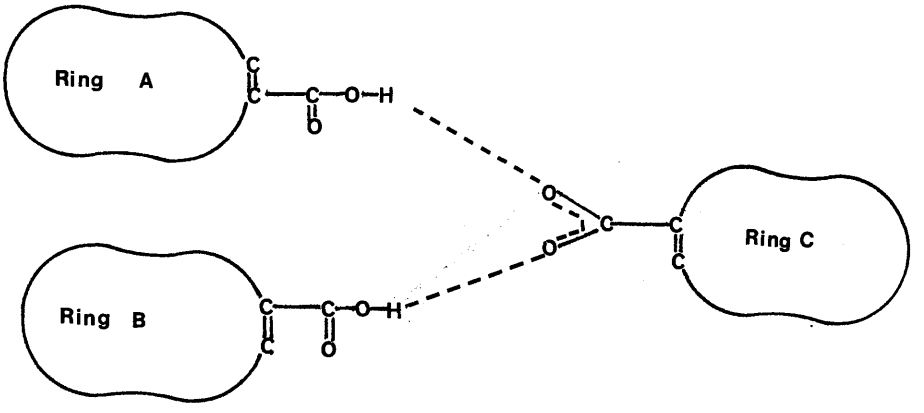
Since the anion and the neutral carboxyl groups are crystallographically different, the compound has been classified as type B rather than type A[13]. Tables 1 and 2 recorded the results of hydrogen atom location by neutron diffraction methods in some crystalline hydrates and some crystalline acid salts. Examination of the corresponding parameters in this crystal analysis discloses short unsymmetrical hydrogen bonds of comparable dimensions.

The most carefully studied acid salt of type B, is rubidium hydrogen bis-glycollate[31], $RbHX_2$, where X = $HO.CH_2.CO_2H$. Some dimensions in this structure are recorded in Table 11 with corresponding dimensions from the present analysis. There is good agreement between the X^- and HX species in both, suggesting that the present work does, indeed, introduce another acid salt with short unsymmetrical hydrogen bonds.

The structure studied here contains two acid units, HX, for every anionic unit, X^-. This is analogous to the aforementioned dihydrogen triacetate, a recent study of which has been undertaken by A.Peratti and V.Tazzoli[30]. They found that, as in

type B hydrogen diacetate salts, two kinds of non-equivalent residues are present: namely, a symmetrical RCO^{-}_{2} anion and two non-symmetrical neutral RCOOH molecules. Comparable distances are recorded in Table 12.

In the present study, the two acid units are each linked by an H bond to an oxygen atom on the X^{-} unit, as indicated in Figure 5.10.



Thetwo strong asymmetrical H bonds have dimensions similar to those found in a type B_2[13] acid salt, namely, potassium dichromate[32] which has been studied by neutron diffraction. Table 13 records dimensions of both ; it also includes available data for sodium dihydrogen triacetate[30], limited by the omission of details concerning the hydrogen atoms.

The values reported in Tables 11 and 13 indicate that the

TABLE 12 : Some interatomic distances (Å) and bond angles (°) for $NaH_2(O_2CCH_3)_3$[30] (III) and for the title compound (II).

For X^- :

	III	II - ring C
C-O	1.256(5)	1.231(6)
C-O	1.265(5)	1.258(6)
O-C-O	122.51(34)	124.6(4)
C-C-O	118.54(43)	119.0(4)
C-C-O	118.94(43)	116.4(5)

For HX :

	III - ring 1	III - ring 2	II - ring A	II - ring B
C=O	1.223(5)	1.213(5)	1.208(6)	1.194(6)
C-OH	1.299(5)	1.300(5)	1.311(6)	1.309(6)
O=C-OH	122.84(40)	122.46(41)	122.4(4)	122.3(4)
C-C=O	122.12(46)	114.75(44)	126.4(4)	124.9(4)
C-C-OH	114.99(43)	112.79(44)	111.2(4)	112.7(4)

TABLE 13 : H bond lengths (Å) and angles (°) for title structure, for a type B_2 acid salt[32], and for $NaH_2(O_2CCH_3)_3$[30].

REFERENCE	O....O	O-H	O-H..O
Present study	2.545(3)	1.04(6)	168
	2.484(3)	0.96(5)	168
32	2.543(8)	1.050(12)	172
	2.554(7)	1.018(12)	163
30	2.503(4)		
	2.509(4)		

present structure fulfils the criteria for the existence of H bonding outlined in the introduction to this chapter. Oxygen acts both as the proton donor and the proton acceptor group; the H bonds are slightly bent with the O-H..O angles having values of 168.0° and 167.5°; and, finally, the total H bond length is equal to, or less than, the sum of the van der Waals radii of the oxygen atoms (taken as 1.4 Å).

Ferraris and Franchini-Angela[33] have made a detailed statistical survey of some ninety water molecules, whose structures have been determined accurately by neutron diffraction, in about forty different crystalline hydrates. One of the correlations published is a histogram of the frequencies of occurrence of various O-H..O angles. As found previously, 180° is not the most common angle: there is a maximum for the range $165\text{-}170^{\circ}$ which has nearly twice as many examples as that found for the range $175\text{-}180^{\circ}$.

Moving to a different aspect of H bonding, the possible forms of the potential energy diagram as the proton varies its position along the internuclear axis between the two oxygen atoms is now considered. For the most general case of a long H bond (O....O > 2.8 Å), the curve has the form shown in Figure 5.1b : the unsymmetrical double minimum with the two energy minima separated by a substantial barrier. The lower minimum corresponds to the covalent attachment of the proton to one of the oxygens and not to the other. For medium H bonds (2.65 < O....O < 2.8 Å), the two minima are equivalent in energy giving rise to a symmetrical double minimum with a substantial barrier between them (Figure 5.1c). There are two possible positions for the proton - about 1.0 Å from either oxygen. As the symmetrically-environed bond becomes shorter (O....O < 2.65 Å), the two energy minima move closer together and the barrier between them becomes lower. At the limit, the barrier has disappeared and we have the symmetrical single minimum (Figure 5.1d) in which the proton would vibrate

harmonically. Somewhere between c and d in Figure 5.1, the barrier will have subsided below the zero-point level of vibrational energy. The effective potential well can, perhaps, be regarded as flattened such that the vibration of the proton along the bond would be anharmonic. It is virtually impossible, by diffraction methods alone, to distinguish between situations c and d, where the two minima are fairly close together.

5.6 DISCUSSION OF THE ELEVEN MEMBERED RING CONFORMATIONS

The crystal structure of the title compound has three cycloundec-1-ene rings in the asymmetric unit. These are referred to as ring A, ring B (for the HX units) and ring C (for the X^- unit). Both HX rings take identical conformations which correspond to the fifth lowest energy cycloundecane conformation predicted in Chapter 2. This is one of the conformations Anet[37] has not included in his conformational treatise on cycloundecanes. Conversion of the cycloundecane low energy conformations to cycloundecene conformations, by conversion of a single C-C bond to a double C=C bond, indicated that this conformation became the minimum energy conformation of all conformations studied. The zerumbone 2,4-DNP derivative reported in the previous chapter also bears a conformational resemblance to the ring A (or B) conformation. Table 14 reports the observed TAs for rings A and B, and compares them to the observed TAs for the zerumbone 2,4-DNP, the calculated TAs for cycloundecane 5 and the calculated TAs for cycloundecene 1. Ring C TAs are also included and it can be readily concluded that ring C has a different conformation from that of ring A (or B).

The pattern of TAs, and hence the conformation, of ring C as a whole, is also distinctly different from the previously observed cycloundecanone[38] and cycloundecane oxime[39] low-temperature studies. There are, however, a number of rather disturbing features in the apparent molecular geometry of ring C. The bond lengths and bond angles lie so far outside their normal ranges as to appear highly implausible. The behaviour of the temperature factors is also quite unusual. The ring atoms of C are associated with highly anisotropic temperature factors; the principal axes of the thermal ellipsoids having Uii values greater than 0.3 Å, corresponding to B values of greater than 8 $Å^2$! The possibility of gross errors in the atomic positions can be more or less excluded on account of the good agreement between observed and calculated F values (R = 0.064). One is forced to conclude either that the atoms in question carry out thermal

vibrations of extremely large amplitude, or else, that the structure is disordered. One could expect that different X^- molecules in the crystal do not have identical conformations, the differences mainly affecting those atoms with the largest apparent temperature factors. In either case, the apparent bond lengths and angles, as calculated from the mean atomic positions, would be in error since it is known that separations between the mean positions of atoms undergoing large thermal motions cannot be interpreted as interatomic distances[40]. The "observed" conformation, in spite of its manifestly unsatisfactory features, can at least be useful as a starting point for strain-minimisation calculations. It is hoped that one could derive from it a conformation of the same general type, but with more reasonable molecular parameters. When this "observed" conformation is minimised with respect to strain energy, it results in a model with reasonable bond lengths and angles and with TAs as indicated in Table 15 (conformation X). The calculated V_s of this X conformation is 10.46 kcal $mole^{-1}$ i.e. it lies between the calculated cycloundecenes 4 and 5 reported in Chapter 2. Conformation X can also be derived from cycloundecane 8 by conversion of the 123° TA (see Figure 2.8) on the long side of the ring into a trans double bond, with subsequent energy minimisation. Included in Table 15, are the TAs for cycloundecene 5 (Cyen 5) and also those of the "observed" conformation. The column labelled 5:X in this table, includes the calculated TAs for a 40:60 ratio of cycloundecene 5 : conformation X which bears a closer resemblance to the "observed" conformation than the separate conformers. Without a complete generation of all possible conformations of cycloundecenes, a more precise fit is impossible.

It is apparent from Table 15 that the TAs about the bonds 1-2, 2-3, 3-4, 4-5, 5-6 and 6-7 are roughly equal in the cycloundecene 5 and cycloundecene X conformations. The differences mainly affect atoms 1, 11, 10, 9 and 8. To a good approximation, the relative positions of the atoms in the

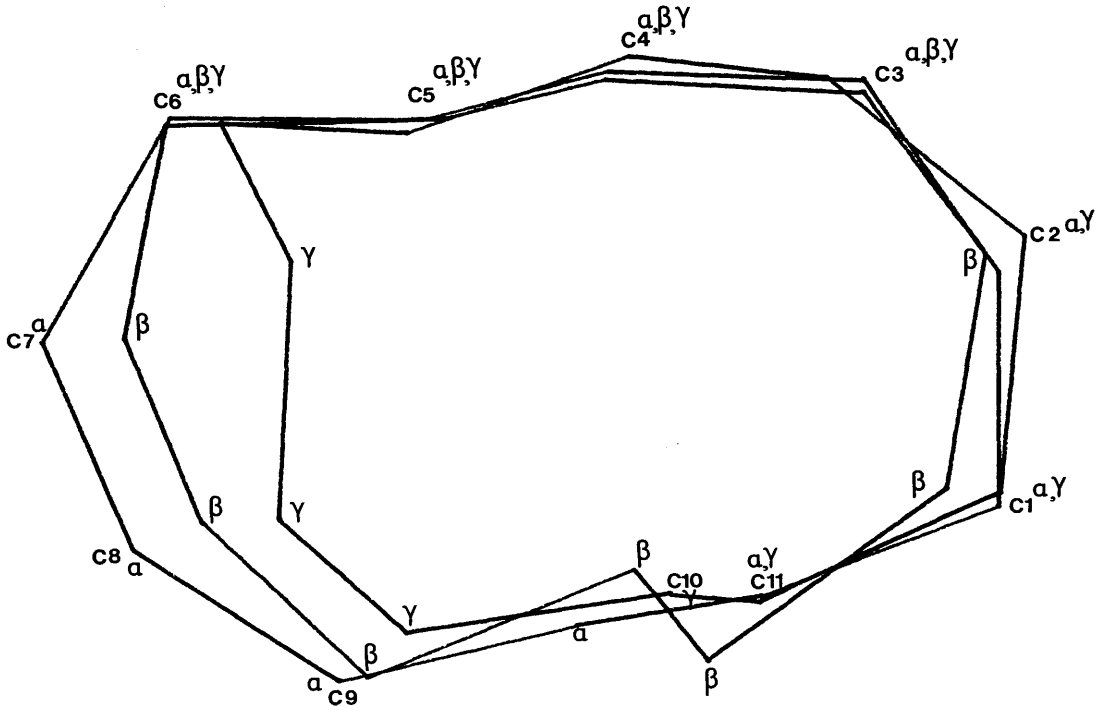
TABLE 15

TA (°)	ring C	X	Cyen 5	5 : X
11-1-2-3	174	177	176	176
1-2-3-4	-121	-114	-116	-115
2-3-4-5	65	90	90	90
3-4-5-6	-53	-48	-46	-47
4-5-6-7	-52	-60	-60	-60
5-6-7-8	155	171	161	165
6-7-8-9	-125	-136	-151	-145
7-8-9-10	51	100	60	76
8-9-10-11	1	-86	52	-3
9-10-11-1	-4	68	-75	-18
10-11-1-2	-73	-125	-59	-86

"observed" conformation lie between those of corresponding atoms in the two calculated rings (cycloundecenes 5 and X) - as shown in Figure 5.11. This suggests that the crystal contains a mixture of the two calculated conformations.

A similar situation arose in an x-ray analysis[41,42] of 4,4,8,8-tetramethylcyclodecane carboxylic acid. The ring conformation was distinctly different from that previously observed and abnormal geometrical values were recorded for part of the ring. MM calculations[43] predicted the "observed" structure to be composed of a mixture of two calculated conformations.

FIG. 5.11 : CYEN X (α), RING C(β), CYEN 5 (γ)



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CHAPTER SIX

X-RAY ANALYSES OF TWO CYCLOUNDECANE DERIVATIVES

6.0 INTRODUCTION

Very little structural information is available for the 11- and higher odd-membered cycloalkanes as evidenced by the publication of only two completed structural analyses for cycloundecane derivatives[1,2], namely, low temperature studies on cycloundecanone[1] and cycloundecane oxime[2].

The former analysis reveals the presence of a single asymmetric structure analogous to the [335] structure, predicted by various workers[3-6] to be a minimum energy conformation. The latter analysis reveals a [12323] conformation predicted by some workers as another minimum energy conformation[3,5,6]. The calculations in this thesis predict the [12323] to be the GMEC.

The present structural analyses introduce two new crystal structures to the medium-ring cycloalkane collection: a cycloundecylmethyl 3,5-dinitrobenzoate (abbreviated to DNZ) and a cycloundecylmethyl naphthylurethane (abbreviated to URETH).

Several conformations of cycloundecane have been calculated to be of approximately the same energy. This agrees with the very complicated low temperature NMR spectrum[7,8] and low melting point.

6.1 EXPERIMENTAL FOR CYCLOUNDECYLMETHYL 3,5-DINITROBENZOATE

The 3,5-dinitrobenzoate derivative of cycloundecylmethanol was prepared by a standard procedure[9] and was recrystallised from ethanol prior to x-ray analysis.

Crystal Data.

Cycloundecylmethyl 3,5-dinitobenzoate, $C_{19}H_{26}N_2O_6$, M = 378.4 amu, monoclinic, $\underline{a}$ = 17.603(0), $\underline{b}$ = 5.254(6), $\underline{c}$ = 21.517(0) Å, β = 96.07(9)°, U = 1979.1 Å^3, z = 4, $D\underline{c}$ = 1.27 g.cm.$^{-3}$, F(000) = 808, Space Group = $P2_1/a$, μ(Mo-Kα) = 1.023 cm.$^{-1}$.

Data Collection.

Instrument used : Enraf-Nonius CAD4 diffractometer.
Radiation used : Mo-Kα, λ = 0.71069 Å.
Monochromation used : graphite crystal.
Upper limit for data collection, Θ_{max} = 23°.
Number of independent observed reflections: m = 1148.
Unobserved cut-off : $2.5\sigma_I$.
Number of parameters refined: n = 270.
Number of reflections per parameter : m/n = 4.25.

Cell dimensions were derived from least-squares refinement of the setting angles for 25 reflections. For intensity measurements, 3216 reflections $\underline{hkl}$ and $\underline{hk\bar{l}}$ were surveyed in the range $\Theta \leqslant 23°$ and 1148 reflections satisfied the criterion, $I > 2.5\sigma_I$.

Structure Analysis.

The structure was solved using the MULTAN[10] suite of programs which incorporates higher invariants i.e. quartets[11]. 3619 quartets were produced using QGEN for the top 100 E-magnitudes with $|E| \geqslant 2.2$ and with $P_7^{\pm} \geqslant 0.6$ and $P_{13}^{\pm} \geqslant 0.7$.

Triplet phase relationships were generated for the top 208 E-magnitudes with $|E| \geq 1.8$. An E-map computed from the set with the lowest NQUEST[11] (-0.88) figure of merit, revealed a 19-atom fragment. Weighted Fourier calculations on this fragment solved for all non-hydrogen atoms. These approximate coordinates were refined with anisotropic thermal parameters via several cycles of full-matrix least-squares calculations using SHELX[12]. A difference synthesis at R = 0.107 revealed all the hydrogen atoms which were subsequently included in further least-squares refinement. This resulted in a final R of 0.075 (R_w = 0.078) using isotropic thermal parameters for the hydrogens and a weighting scheme of $w = 1/\sigma^2$ ($\underline{F}$).

6.2 RESULTS FOR CYCLOUNDECYLMETHYL 3,5-DINITROBENZOATE

Final structure factors (observed and calculated) are included in the appendices.

TABLE 1 : Fractional atomic coordinates (x/a, y/b, z/c) ($x10^4$)with esd's in parentheses for non-hydrogen atoms.

TABLE 2 : Thermal parameters (U_{11}, U_{22}, U_{33}, U_{23}, U_{13}, U_{12}) ($x10^3$) ($Å^2$) for non-hydrogen atoms.

TABLE 3 : Fractional atomic coordinates ($x10^3$) and U isotropic ($x10^3$) ($Å^2$) for hydrogen atoms.

TABLE 4 : Interatomic bonded distances (Å).

TABLE 5 : Valence angles (°).

TABLE 6 : Torsion angles (°).

TABLE 1

C(1)	3918(4)	4260(15)	2458(4)
C(2)	3194(5)	5839(17)	2564(4)
C(3)	2942(7)	5824(19)	3224(5)
C(4)	2667(8)	3279(18)	3419(6)
C(5)	2567(12)	3027(31)	4128(7)
C(6)	3271(14)	3364(32)	4582(8)
C(7)	3916(17)	1611(33)	4587(10)
C(8)	4633(16)	3206(32)	4247(11)
C(9)	4700(20)	1735(41)	3791(11)
C(10)	5107(9)	3153(36)	3225(7)
C(11)	4621(6)	5136(19)	2887(5)
C(12)	4028(5)	4475(17)	1781(4)
C(13)	5529(4)	1007(14)	1001(4)
C(14)	5786(4)	-0687(16)	1499(3)
C(15)	6348(4)	-2352(14)	1363(4)
C(16)	6648(4)	-2508(14)	0804(4)
C(17)	6368(4)	-0795(15)	0355(3)
C(18)	5811(4)	1010(14)	0429(3)
C(19)	4901(4)	2967(15)	1123(4)
N(1)	6628(4)	-4220(15)	1866(4)
N(2)	6671(4)	-0865(14)	-0252(3)
O(1)	4670(3)	2787(10)	1677(2)
O(2)	4652(3)	4351(11)	0697(3)
O(11)	6400(4)	-3960(15)	2370(3)
O(12)	7088(4)	-5788(13)	1736(3)
O(21)	7162(3)	-2488(11)	-0337(3)
O(22)	6430(3)	0611(11)	-0661(3)

TABLE 2

C(1)	82(6)	41(5)	74(5)	-5(4)	10(4)	5(4)
C(2)	96(7)	55(5)	96(6)	-12(5)	39(6)	13(5)
C(3)	118(9)	67(6)	140(9)	7(6)	48(8)	6(6)
C(4)	173(14)	65(7)	159(11)	-35(7)	75(10)	-33(7)
C(5)	262(20)	130(13)	125(11)	-59(10)	96(13)	-66(13)
C(6)	379(33)	100(12)	124(12)	-12(10)	101(17)	-36(16)
C(7)	418(38)	63(10)	235(22)	42(12)	55(22)	8(16)
C(8)	372(30)	92(13)	269(22)	-110(16)	-131(24)	81(17)
C(9)	424(41)	122(15)	238(22)	-13(18)	-73(29)	121(21)
C(10)	135(12)	208(17)	134(10)	33(12)	-7(9)	21(12)
C(11)	103(7)	75(6)	102(7)	-14(6)	5(6)	18(6)
C(12)	86(6)	71(6)	70(5)	-7(5)	26(5)	21(5)
C(13)	50(4)	37(4)	83(5)	-9(4)	7(4)	-6(4)
C(14)	61(5)	54(5)	61(5)	2(4)	11(4)	-11(4)
C(15)	54(4)	35(4)	80(5)	17(4)	6(4)	-4(4)
C(16)	55(4)	39(4)	82(5)	-5(5)	10(4)	-10(4)
C(17)	61(5)	48(4)	60(5)	5(4)	13(4)	-11(5)
C(18)	55(5)	41(4)	75(6)	-11(4)	21(4)	-1(4)
C(19)	69(5)	47(5)	53(5)	-5(4)	1(4)	-2(4)
N(1)	75(5)	76(5)	78(5)	17(5)	11(4)	-3(5)
N(2)	61(4)	61(4)	73(5)	-1(4)	12(4)	2(4)
O(1)	96(4)	64(3)	70(4)	-6(3)	28(3)	23(3)
O(2)	94(4)	70(4)	79(4)	11(3)	26(3)	17(4)
O(11)	112(5)	122(6)	95(5)	52(4)	34(4)	30(4)
O(12)	123(5)	67(4)	127(6)	25(4)	20(5)	34(4)
O(21)	88(4)	74(4)	99(4)	3(4)	27(3)	24(4)
O(22)	93(4)	77(4)	75(4)	21(3)	9(3)	15(4)

TABLE 3

H(1)	384(0)	229(1)	258(0)	124(33)
H(21)	273(1)	510(2)	225(0)	119(34)
H(22)	330(1)	779(2)	244(0)	136(36)
H(31)	248(1)	718(2)	324(1)	143(38)
H(32)	342(1)	639(2)	355(1)	167(52)
H(41)	212(1)	291(2)	316(1)	239(84)
H(42)	307(1)	186(2)	331(1)	112(30)
H(51)	234(1)	115(3)	420(1)	280(85)
H(52)	216(1)	444(3)	424(1)	337(130)
H(61)	309(1)	331(3)	505(1)	168(42)
H(62)	349(1)	523(3)	449(1)	258(81)
H(71)	411(2)	107(3)	506(1)	668(127)
H(72)	374(2)	-007(3)	432(1)	291(94)
H(81)	515(2)	330(3)	456(1)	207(66)
H(82)	446(2)	510(3)	410(1)	183(51)
H(91)	505(2)	013(4)	395(1)	110(29)
H(92)	414(2)	108(4)	361(1)	222(92)
H(101)	523(1)	172(4)	289(1)	886(124)
H(102)	563(1)	403(4)	342(1)	223(71)
H(111)	442(1)	638(2)	323(0)	108(30)
H(112)	498(1)	619(2)	260(0)	125(36)
H(121)	416(0)	641(2)	167(0)	122(31)
H(122)	352(0)	389(2)	150(0)	68(19)
H(14)	556(0)	-066(2)	195(0)	88(24)
H(16)	708(0)	-389(1)	072(0)	85(24)
H(18)	561(0)	233(1)	006(0)	239(71)

TABLE 4

C(1) - C(2)	1.557(12)	C(13) - C(18)	1.377(11)
C(1) - C(11)	1.533(13)	C(13) - C(19)	1.552(10)
C(1) - C(12)	1.495(11)	C(14) - C(15)	1.375(10)
C(2) - C(3)	1.533(14)	C(15) - C(16)	1.365(11)
C(3) - C(4)	1.497(15)	C(15) - N(1)	1.504(11)
C(4) - C(5)	1.56(2)	C(16) - C(17)	1.373(11)
C(5) - C(6)	1.51(3)	C(17) - C(18)	1.386(10)
C(6) - C(7)	1.46(3)	C(17) - N(2)	1.463(10)
C(7) - C(8)	1.74(4)	C(19) - O(1)	1.303(10)
C(8) - C(9)	1.27(3)	C(19) - O(2)	1.215(10)
C(9) - C(10)	1.65(3)	N(1) - O(11)	1.204(11)
C(10) - C(11)	1.49(2)	N(1) - O(12)	1.208(11)
C(12) - O(1)	1.473(10)	N(2) - O(21)	1.242(9)
C(13) - C(14)	1.428(11)	N(2) - O(22)	1.214(9)

TABLE 5

C(11)	C(1)	C(2)	111.9(7)	C(12)	C(1)	C(2)	107.1(6)
C(3)	C(2)	C(1)	117.0(7)	C(12)	C(1)	C(11)	112.6(7)
C(10)	C(11)	C(1)	118.0(10)	O(1)	C(12)	C(1)	106.4(6)
C(4)	C(3)	C(2)	113.5(9)	C(5)	C(4)	C(3)	115.1(1[illegible])
C(6)	C(5)	C(4)	117.1(16)	C(7)	C(6)	C(5)	121.[illegible](16)
C(8)	C(7)	C(6)	106.9(15)	C(9)	C(8)	C(7)	99.4(2[illegible])
C(10)	C(9)	C(8)	112.3(19)	C(11)	C(10)	C(9)	113.[illegible](15)
C(19)	O(1)	C(12)	114.5(6)	C(18)	C(13)	C(14)	123.[illegible](7)
C(19)	C(13)	C(14)	117.5(7)	C(15)	C(14)	C(13)	114.6(7)
C(19)	C(13)	C(18)	118.7(7)	C(17)	C(18)	C(13)	115.3(7)
O(1)	C(19)	C(13)	113.7(7)	O(2)	C(19)	C(13)	118.5(7)
C(16)	C(15)	C(14)	125.4(7)	N(1)	C(15)	C(14)	116.[illegible](7)
N(1)	C(15)	C(16)	117.8(6)	C(17)	C(16)	C(15)	115.9(7)
O(11)	N(1)	C(15)	117.3(7)	O(12)	N(1)	C(15)	117.1(7)
C(18)	C(17)	C(16)	125.0(7)	N(2)	C(17)	C(16)	118.4(7)
N(2)	C(17)	C(18)	116.6(6)	O(21)	N(2)	C(17)	118.3(7)
O(22)	N(2)	C(17)	119.9(7)	O(2)	C(19)	O(1)	127.6(7)
O(12)	N(1)	O(11)	125.5(8)	O(22)	N(2)	O(21)	121.[illegible](7)

TABLE 6

C(11)	C(1)	C(2)	C(3)	-58.6(10)	C(12)	C(1)	C(2)	C(3)	177.5(8)
C(2)	C(1)	C(11)	C(10)	133.5(10)	C(12)	C(1)	C(11)	C(10)	-105.8(11)
C(2)	C(1)	C(12)	O(1)	-174.9(6)	C(11)	C(1)	C(12)	O(1)	61.7(8)
C(1)	C(2)	C(3)	C(4)	-66.7(11)	C(2)	C(3)	C(4)	C(5)	167.5(11)
C(3)	C(4)	C(5)	C(6)	-61.6(18)	C(4)	C(5)	C(6)	C(7)	-63.3(24)
C(5)	C(6)	C(7)	C(8)	105.3(20)	C(6)	C(7)	C(8)	C(9)	-119.7(22)
C(7)	C(8)	C(9)	C(10)	159.5(18)	C(8)	C(9)	C(10)	C(11)	-69.4(23)
C(9)	C(10)	C(11)	C(1)	-70.8(17)	C(1)	C(12)	O(1)	C(19)	-178.4(6)
C(18)	C(13)	C(14)	C(15)	0.0(11)	C(19)	C(13)	C(14)	C(15)	-179.3(7)
C(14)	C(13)	C(18)	C(17)	0.8(11)	C(19)	C(13)	C(18)	C(17)	-179.1(8)
C(14)	C(13)	C(19)	O(1)	-1.2(10)	C(14)	C(13)	C(19)	O(2)	-176.9(7)
C(18)	C(13)	C(19)	O(1)	179.5(7)	C(18)	C(13)	C(19)	O(2)	3.8(11)
C(13)	C(14)	C(15)	C(16)	-1.4(11)	C(13)	C(14)	C(15)	N(1)	-178.7(6)
C(14)	C(15)	C(16)	C(17)	1.7(11)	N(1)	C(15)	C(16)	C(17)	179.0(7)
C(14)	C(15)	N(1)	O(11)	-7.4(11)	C(14)	C(15)	N(1)	O(12)	175.6(7)
C(16)	C(15)	N(1)	O(11)	175.0(8)	C(16)	C(15)	N(1)	O(12)	-1.9(11)
C(15)	C(16)	C(17)	C(18)	-0.7(11)	C(15)	C(16)	C(17)	N(2)	179.8(7)
C(16)	C(17)	C(18)	C(13)	-0.4(11)	N(2)	C(17)	C(18)	C(13)	179.1(6)
C(16)	C(17)	N(2)	O(21)	0.7(10)	C(16)	C(17)	N(2)	O(22)	179.4(7)
C(18)	C(17)	N(2)	O(21)	-178.8(7)	C(18)	C(17)	N(2)	O(22)	-0.1(10)
C(13)	C(19)	O(1)	C(12)	-174.8(6)	O(2)	C(19)	O(1)	C(12)	0.3(11)

6.3 EXPERIMENTAL FOR CYCLOUNDECYLMETHYL NAPHTHYLURETHANE

The sample compound was prepared by a standard procedure from cycloundecylmethanol and was recrystallised from ethanol.

Crystal Data.

Cycloundecylmethyl α-naphthylurethane, $C_{23}H_{31}NO_2$, M = 353.5 amu, monoclinic, a = 8.789(3), b = 26.393(4), c = 9.237(2) Å, $\beta = 107.33(2)^\circ$, U = 2045.42 Å^3, z = 4, Dc = 1.15 g.cm.$^{-3}$, F(000) = 768, Space Group = $P2_1/c$, μ(Cu-Kα) = 6.897 cm.$^{-1}$

Data Collection.

Instrument used : Enraf-Nonius CAD4 diffractometer.
Radiation used : Cu-Kα, λ = 1.5418 Å.
Monochromation used : graphite crystal.
Upper limit for data collection : $\Theta_{max} = 72^\circ$.
Number of independent observed reflections : m = 2288.
Unobserved cut-off : $2.5\sigma_I$.
Number of parameters refined : n = 269.
Number of reflections per parameter : m/n = 8.5.

Least-squares refinement of the setting angles for 25 reflections produced the cell dimensions. 4013 reflections hkl and hk$\bar{l}$ were surveyed in the range $\Theta \leqslant 72^\circ$ and satisfied the condition, $I > 2.5\sigma_I$.

Structure Analysis.

The multi-option program MULTAN[10] produced four phase sets which were calculated for the top 204 E-magnitudes, $|E| \geqslant 2.00$. An E-map computed from the set showing the highest combined figure of merit revealed an 18-atom fragment. Weighted Fourier and SHELX[12] full-matrix least-squares calculations solved for all non-hydrogen atoms. A difference synthesis at R = 0.124

revealed all the hydrogen atoms which were included in further least-squares refinement with isotropic temperature factors. This resulted in a final R value of 0.079 (R_w = 0.097). The weighting scheme employed in the final stages of refinement was w = $1/\sigma^2$ ($\underline{F}$).

6.4 RESULTS FOR CYCLOUNDECYLMETHYL α-NAPHTHYLURETHANE

Final structure factors (observed and calculated) are included in the appendices.

TABLE 7 : Fractional atomic coordinates (x/a, y/b, z/c) ($x10^4$) with esd's in parentheses for non-hydrogen atoms.

TABLE 8 : Thermal parameters (U_{11}, U_{22}, U_{33}, U_{23}, U_{13}, U_{12}) ($x10^3$) ($Å^2$) for non-hydrogen atoms.

TABLE 9 : Fractional atomic coordinates ($x10^3$) with U isotropic ($x10^3$) ($Å^2$) for hydrogen atoms.

TABLE 10 : Interatomic bonded distances (Å).

TABLE 11 : Valence angles (°).

TABLE 12 : Torsion angles (°).

ORTEP[13] representations of cycloundecylmethyl 3,5-dinitobenzoate and cycloundecylmethyl naphthylurethane are given in Figures 6.1 and 6.2, respectively.

TABLE 7

C(1)	3376(5)	1433(1)	9539(4)
C(2)	4786(7)	1791(2)	10112(6)
C(3)	4825(11)	2122(3)	11340(11)
C(4)	4972(16)	1833(5)	12925(13)
C(5)	6534(14)	1792(7)	13401(21)
C(6)	5937(20)	1404(9)	14763(10)
C(7)	6190(16)	0865(6)	14563(12)
C(8)	5625(14)	0420(4)	13507(12)
C(9)	4166(10)	0539(2)	11781(10)
C(10)	5110(11)	0651(3)	10894(11)
C(11)	3863(9)	0888(2)	9343(6)
C(12)	2330(6)	1603(2)	8026(4)
C(13)	1027(5)	2366(1)	7000(3)
C(14)	-0096(4)	3229(1)	6449(3)
C(15)	0124(4)	3720(1)	7086(4)
C(16)	0927(5)	3824(1)	8624(4)
C(17)	1060(6)	4307(2)	9166(5)
C(18)	0436(7)	4713(2)	8219(6)
C(19)	-0305(6)	4635(2)	6763(7)
C(20)	-0507(5)	4141(2)	6117(4)
C(21)	-1297(6)	4059(2)	4580(5)
C(22)	-1484(6)	3584(2)	4025(5)
C(23)	-0886(5)	3154(2)	4959(4)
N(1)	0547(4)	2814(1)	7409(3)
O(1)	1769(4)	2102(1)	8233(2)
O(13)	0856(4)	2213(1)	5725(3)

TABLE 8

C(1)	119(3)	75(2)	75(2)	-5(2)	28(2)	14(2)
C(2)	139(5)	100(3)	128(4)	-10(3)	18(3)	2(3)
C(3)	176(7)	156(6)	191(7)	-58(6)	-7(6)	25(5)
C(4)	246(13)	250(11)	227(11)	-87(9)	35(9)	102(10)
C(5)	142(6)	505(25)	470(24)	-322(22)	141(12)	-123(12)
C(6)	308(18)	591(31)	115(6)	-23(12)	35(7)	227(19)
C(7)	280(14)	335(17)	125(7)	78(9)	17(8)	123(13)
C(8)	279(12)	245(10)	159(7)	82(7)	59(7)	110(10)
C(9)	163(6)	97(4)	315(10)	38(5)	138(7)	1(4)
C(10)	201(8)	103(4)	359(12)	-72(6)	158(9)	-10(5)
C(11)	182(6)	94(3)	105(3)	-6(3)	15(3)	47(4)
C(12)	141(4)	80(2)	75(2)	-7(2)	36(2)	22(3)
C(13)	97(3)	77(2)	55(2)	0(2)	27(2)	-8(2)
C(14)	69(2)	83(2)	60(2)	9(2)	23(2)	-1(2)
C(15)	74(2)	76(2)	70(2)	8(2)	29(2)	1(2)
C(16)	104(3)	82(2)	80(2)	4(2)	35(2)	-1(2)
C(17)	136(4)	79(3)	103(3)	-11(2)	37(3)	-3(3)
C(18)	141(4)	80(3)	128(4)	0(3)	55(3)	0(3)
C(19)	117(4)	84(3)	143(4)	28(3)	68(3)	16(3)
C(20)	79(3)	90(3)	91(3)	23(2)	37(2)	8(2)
C(21)	102(3)	114(3)	97(3)	36(3)	29(2)	18(3)
C(22)	104(3)	138(4)	74(2)	24(3)	11(2)	13(3)
C(23)	92(3)	110(3)	68(2)	3(2)	18(2)	0(2)
N(1)	110(3)	74(2)	52(2)	0(1)	27(2)	4(2)
O(1)	145(3)	85(2)	61(1)	3(1)	34(1)	28(2)
O(13)	163(3)	89(2)	56(1)	-7(1)	36(1)	3(2)

TABLE 9

H(1)	277(1)	144(0)	1039(0)	91(11)
H(2A)	483(1)	203(0)	917(1)	235(33)
H(2B)	585(1)	156(0)	1046(1)	175(22)
H(3A)	584(1)	237(0)	1151(1)	733(46)
H(3B)	374(1)	234(0)	1104(1)	203(27)
H(4A)	439(2)	147(0)	1275(1)	491(46)
H(4B)	452(2)	206(0)	1368(1)	290(45)
H(5A)	709(1)	160(1)	1266(2)	184(23)
H(5B)	720(1)	213(1)	1383(2)	510(46)
H(6A)	469(2)	147(1)	1462(1)	347(48)
H(6B)	662(2)	152(1)	1589(1)	706(46)
H(7A)	744(2)	087(1)	1464(1)	390(47)
H(7B)	604(2)	072(1)	1560(1)	186(24)
H(8A)	665(1)	026(0)	1325(1)	650(45)
H(8B)	515(1)	014(0)	1411(1)	650(45)
H(9A)	341(1)	085(0)	1186(1)	159(19)
H(9B)	344(1)	021(0)	1137(1)	162(20)
H(10A)	601(1)	093(0)	1144(1)	174(21)
H(10B)	568(1)	031(0)	1064(1)	130(14)
H(11A)	280(1)	060(0)	902(1)	256(39)
H(11B)	443(1)	088(0)	845(1)	384(46)
H(121)	134(1)	135(0)	762(0)	165(21)
H(122)	300(1)	162(0)	722(0)	159(19)
H(16)	144(1)	352(0)	938(0)	116(13)
H(17)	166(1)	438(0)	1035(1)	183(23)
H(18)	056(1)	509(0)	867(1)	147(17)
H(19)	-077(1)	496(0)	604(1)	140(16)
H(21)	-176(1)	438(0)	384(1)	141(16)
H(22)	-211(1)	353(0)	284(0)	112(12)
H(23)	-106(0)	278(0)	449(0)	76(10)
H(N1)	076(5)	282(1)	829(5)	95(14)

TABLE 10

C(1) - C(2)	1.522(7)	C(13) - O(1)	1.329(4)
C(1) - C(11)	1.527(7)	C(13) - O(13)	1.211(4)
C(1) - C(12)	1.495(5)	C(14) - C(15)	1.412(5)
C(2) - C(3)	1.425(10)	C(14) - C(23)	1.359(5)
C(3) - C(4)	1.621(15)	C(14) - N(1)	1.416(4)
C(4) - C(5)	1.316(17)	C(15) - C(16)	1.413(5)
C(5) - C(6)	1.82(2)	C(15) - C(20)	1.432(5)
C(6) - C(7)	1.46(3)	C(16) - C(17)	1.361(6)
C(7) - C(8)	1.513(18)	C(17) - C(18)	1.389(7)
C(8) - C(9)	1.751(14)	C(18) - C(19)	1.324(8)
C(9) - C(10)	1.361(13)	C(19) - C(20)	1.422(6)
C(10) - C(11)	1.645(11)	C(20) - C(21)	1.399(6)
C(12) - O(1)	1.440(5)	C(21) - C(22)	1.347(7)
C(13) - N(1)	1.347(5)	C(22) - C(23)	1.427(6)

TABLE 11

C(11) - C(1) - C(2)	113.4(4)	C(12) - C(1) - C(2)	110.5(4)
C(3) - C(2) - C(1)	118.8(6)	C(12) - C(1) - C(11)	106.7(3)
C(10) - C(11) - C(1)	113.1(4)	O(1) - C(12) - C(1)	106.6(5)
C(4) - C(3) - C(2)	114.0(7)	C(5) - C(4) - C(3)	97.8(11)
C(6) - C(5) - C(4)	77.9(10)	C(7) - C(6) - C(5)	112.6(11)
C(8) - C(7) - C(6)	143.6(11)	C(9) - C(8) - C(7)	117.3(9)
C(10) - C(9) - C(8)	100.1(7)	C(11) - C(10) - C(9)	103.9(7)
C(13) - O(1) - C(12)	117.8(3)	O(1) - C(13) - N(1)	109.5(3)
O(13) - C(13) - N(1)	127.3(3)	C(14) - N(1) - C(13)	127.1(3)
O(13) - C(13) - O(1)	123.1(3)	C(23) - C(14) - C(15)	121.4(3)
N(1) - C(14) - C(15)	116.0(3)	C(16) - C(15) - C(14)	124.3(3)
C(20) - C(15) - C(14)	118.2(3)	N(1) - C(14) - C(23)	120.7(3)
C(22) - C(23) - C(14)	118.8(4)	C(20) - C(15) - C(16)	117.5(3)
C(17) - C(16) - C(15)	121.0(4)	C(19) - C(20) - C(15)	116.2(4)
C(21) - C(20) - C(15)	119.8(4)	C(18) - C(17) - C(16)	121.6(4)
C(19) - C(18) - C(17)	120.2(4)	C(20) - C(19) - C(18)	122.0(4)
C(21) - C(20) - C(19)	122.0(4)	C(22) - C(21) - C(20)	119.8(4)
C(23) - C(22) - C(21)	122.0(4)		

TABLE 12

C(11) - C(1) - C(2) - C(3)	-132.2(6)	C(12) - C(1) - C(2) - C(3)	108.1(6)
C(2) - C(1) - C(11) - C(10)	54.9(6)	C(12) - C(1) - C(11) - C(10)	176.8(5)
C(2) - C(1) - C(12) - O(1)	-60.6(4)	C(11) - C(1) - C(12) - O(1)	175.6(3)
C(1) - C(2) - C(3) - C(4)	65.2(9)	C(2) - C(3) - C(4) - C(5)	85.9(11)
C(3) - C(4) - C(5) - C(6)	-171.1(9)	C(4) - C(5) - C(6) - C(7)	109.4(14)
C(5) - C(6) - C(7) - C(8)	-68.3(25)	C(6) - C(7) - C(8) - C(9)	3.8(26)
C(7) - C(8) - C(9) - C(10)	89.7(11)	C(8) - C(9) - C(10) - C(11)	-168.2(6)
C(9) - C(10) - C(11) - C(1)	77.0(7)	C(1) - C(12) - O(1) - C(13)	169.2(3)
O(1) - C(13) - N(1) - C(14)	171.1(3)	O(13) - C(13) - N(1) - C(14)	-7.9(6)
N(1) - C(13) - O(1) - C(12)	178.2(3)	O(13) - C(13) - O(1) - C(12)	-2.8(5)
C(23) - C(14) - C(15) - C(16)	179.8(4)	C(23) - C(14) - C(15) - C(20)	-0.0(5)
N(1) - C(14) - C(15) - C(16)	-0.9(5)	N(1) - C(14) - C(15) - C(20)	179.3(3)
C(15) - C(14) - C(23) - C(22)	0.8(6)	N(1) - C(14) - C(23) - C(22)	-178.6(4)
C(15) - C(14) - N(1) - C(13)	-152.4(3)	C(23) - C(14) - N(1) - C(13)	27.0(5)
C(14) - C(15) - C(16) - C(17)	-178.4(4)	C(20) - C(15) - C(16) - C(17)	1.4(6)
C(14) - C(15) - C(20) - C(19)	179.1(4)	C(14) - C(15) - C(20) - C(21)	-0.9(5)
C(16) - C(15) - C(20) - C(19)	-0.7(5)	C(16) - C(15) - C(20) - C(21)	179.3(4)
C(15) - C(16) - C(17) - C(18)	-1.1(7)	C(16) - C(17) - C(18) - C(19)	0.0(8)
C(17) - C(18) - C(19) - C(20)	0.7(8)	C(18) - C(19) - C(20) - C(15)	-0.3(7)
C(18) - C(19) - C(20) - C(21)	179.7(5)	C(15) - C(20) - C(21) - C(22)	1.2(7)
C(19) - C(20) - C(21) - C(22)	-178.8(4)	C(20) - C(21) - C(22) - C(23)	-0.5(7)
C(21) - C(22) - C(23) - C(14)	-0.5(7)		

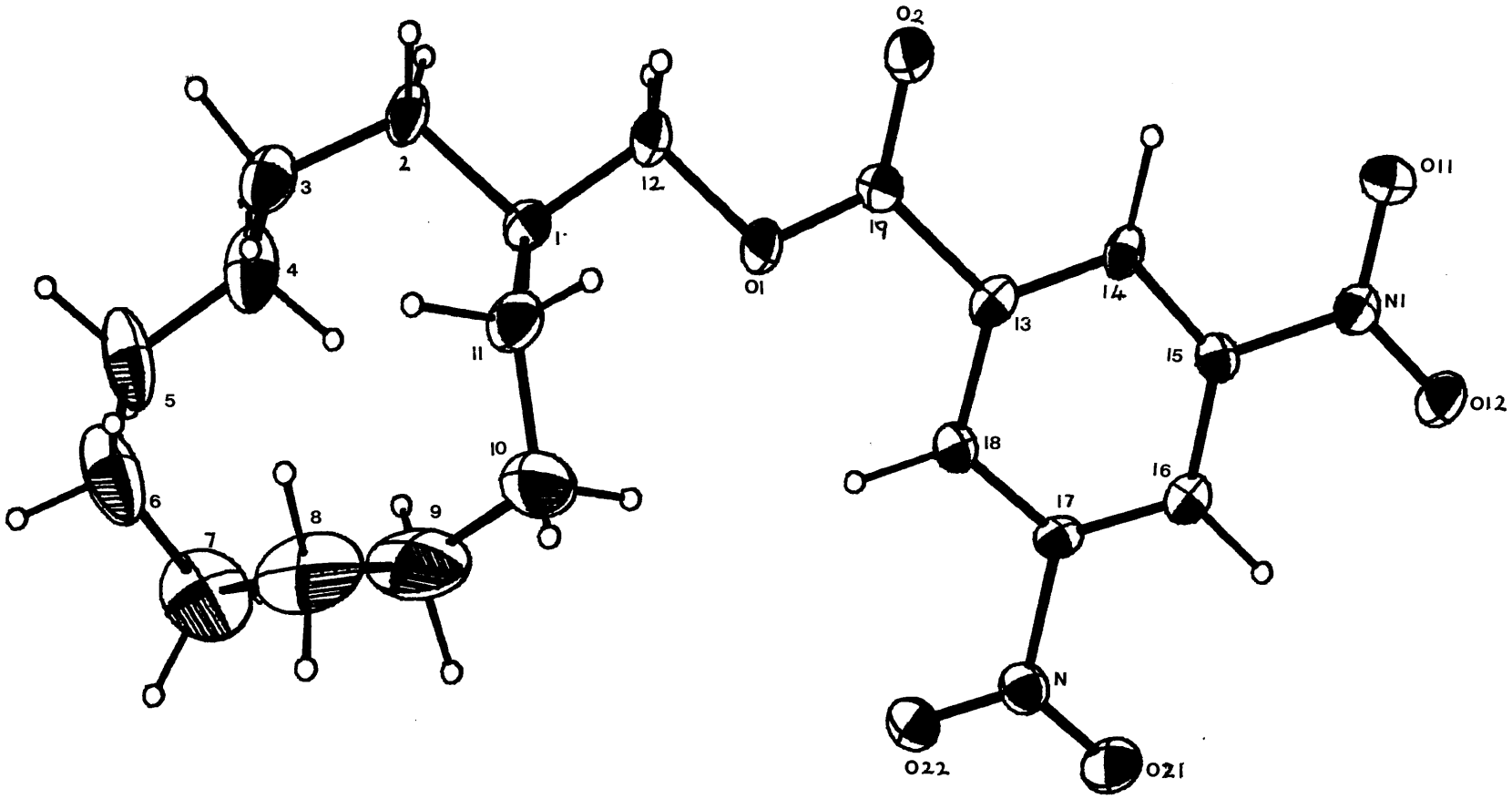

FIG. 6.1

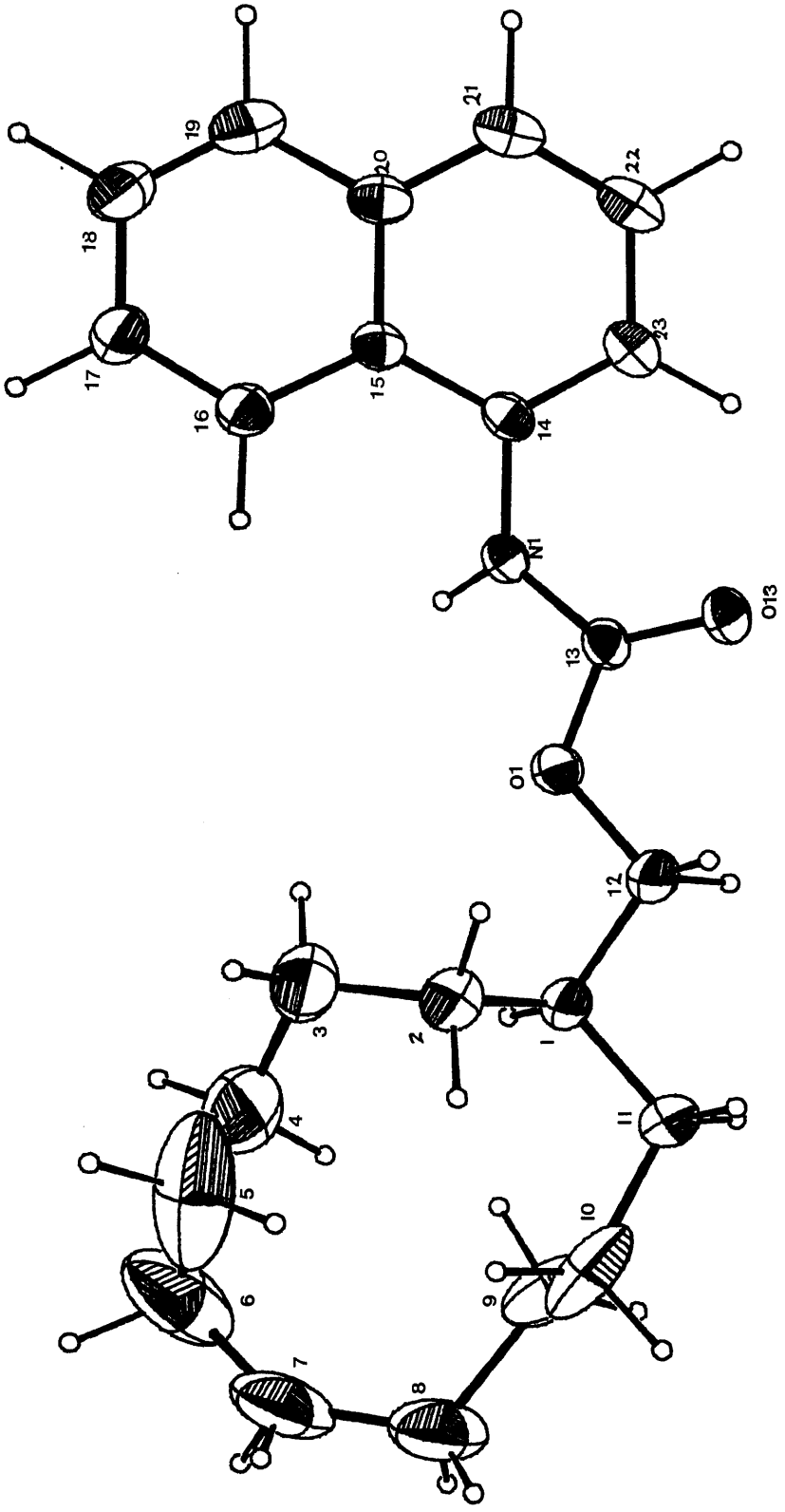

FIG. 6.2.

6.5 DISCUSSION OF RESULTS

Both 11-membered rings in the two crystal structures reported here exhibit some disorder, indicated by the presence of unusually high thermal parameters for specific carbons in the cycloalkane.

DNZ bears a close resemblance to the [335] structure of the calculated conformer - cycloundecane 2, and also to the crystal structure reported for cycloundecanone[1]. Torsion angles for the 11-membered rings of DNZ, cycloundecane 2 (Cyan 2) and cycloundecanone (Cy-one) are listed in Table 13, while their bond angles and bond lengths are recorded in Table 14. The numbering system refers to that used for DNZ in Figure 6.1. Disorder is greatest for carbon atoms 4, 5, 6, 7, 8 and 9, as shown by distortions in bond angles and bond distances for this section of the ring.

The observed conformation for the cycloundecane ring of URETH is even more disordered than that observed for DNZ. Preliminary examination of the TAs of URETH does not readily afford a conformational counterpart from the calculated low energy conformations of cycloundecane. The large deviations of observed bond lengths and angles from expected values are considered to be unreal and to arise only as a result of disorder of the ring. These disorder effects are especially pronounced for carbon atoms 4, 5, 6, 7, 8, 9 and 10, and it is here that the ring clearly assumes different orientations. It is interesting to note that the calculated conformations of cycloundecane 1, 2 and3 are similar over several atoms, which readily correlate to the more ordered section of the cycloundecane ring in URETH - see Table 15. It follows that the section of the 11-membered ring of URETH which shows the greatest distortion corresponds to the region where conformational differences arise among the calculated cycloundecanes - 1, 2 and 3.

TABLE 13 : Ring TAs (°) for DNZ, Cycloundecane 2 (Cyan 2) and Cycloundecanone[1] (Cy-one).

TA	DNZ	Cyan 2	Cy-one
2-3-4-5*	168	171	173
3-4-5-6	-67	-62	-63
4-5-6-7	-59	-65	-64
5-6-7-8	133	137	140
6-7-8-9	-71	-62	-61
7-8-9-10	-69	-62	-60
8-9-10-11	159	158	160
9-10-11-1	-120	-123	-127
10-11-1-2	105	98	95
11-1-2-3	-63	-57	-55
1-2-3-4	-62	-64	-65

* : numbering system refers to that used in DNZ.

TABLE 14 : Ring valence angles (°) and bond lengths (Å) for DNZ, Cycloundecane 2 (Cyan 2), and Cycloundecanone[1] (Cy-one).

ANGLE	DNZ	Cyan 2	Cy-one
11-1-2	111.9(7)	114.5	114.6
1-2-3	117.0(7)	114.2	116.0
2-3-4	113.5(9)	115.7	115.6
3-4-5	115.1(10)	113.7	114.0
4-5-6	117.1(16)	114.5	114.2
5-6-7	121.0(16)	116.6	113.8
6-7-8	106.9(15)	115.9	115.4
7-8-9	99.4(20)	113.5	113.8
8-9-10	112.3(19)	113.6	114.3
9-10-11	113.8(15)	113.9	119.3
10-11-1	118.0(10)	115.7	113.9

BOND	DNZ	Cyan 2	Cy-one
1-2	1.557(12)	1.533	1.522
2-3	1.533(14)	1.534	1.527
3-4	1.497(15)	1.534	1.523
4-5	1.56(2)	1.530	1.537
5-6	1.51(3)	1.531	1.540
6-7	1.46(3)	1.535	1.536
7-8	1.74(4)	1.535	1.528
8-9	1.27(3)	1.532	1.532
9-10	1.65(3)	1.530	1.515
10-11	1.49(2)	1.530	1.516
11-1	1.533(13)	1.535	1.538

Numbering system refers to that used in DNZ.

TABLE 15 : Ring TAs (°) for URETH and Cycloundecanes 1, 2 and 3 (Cyans 1, 2 and 3).

TA	URETH	Cyan 1	Cyan 2	Cyan 3
10-11-1-2	-55	-81	-62	-86
11-1-2-3	132	128	137	127
1-2-3-4	-65	-68	-65	-71
2-3-4-5	-86	-75	-62	-82
3-4-5-6	171	164	171	167
4-5-6-7	-109	-57	-64	-94
5-6-7-8	68	-69	-57	68
6-7-8-9	-4	76	98	-88
7-8-9-10	-90	64	-123	156
8-9-10-11	168	-163	158	-154
9-10-11-1	-77	93	-62	83

Numbering system refers to that used for URETH.

When DNZ and URETH are used as starting-points for strain energy minimisation calculations, convergence occurs for both to models with reasonable bond lengths and angles. These model structures are the same as that calculated for cycloundecane 2 i.e. the [335] conformer of second lowest energy. However, as shown in Chapter 2, there is only a small energy difference between this conformation and the GMEC. The introduction of a single substituent, or lattice effects, may change the order of stability of the conformations.

It has been suggested in Chapter 2, that at room temperature, cycloundecane consists of a mixture of conformations. It is not surprising, therefore, to find disorder in both the DNZ and URETH crystal analyses at this temperature, andit is suggested that this results from the 11-membered rings being conformationally labile. This type of disorder has been observed for other cycloalkanes: the observed arrangement in a crystal analysis for cyclododecane[14] is equally compatible with two different conformations of the individual molecules. Similarly, an x-ray analysis of 4,4,8,8-tetramethylcyclodecanecarboxylic acid[15,16] exhibits a number of disturbing features in the apparent molecular geometry but has good agreement between observed and calculated structure factors. The disorder is rationalised by the suggestion that the crystal actually contains a mixture of two conformations.

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APPENDIX A

AN INVESTIGATION OF THE LOW ENERGY CONFORMATIONS OF 1,4,7,10-CYCLODODECATETRAENES

A.0 INTRODUCTION

This appendix introduces some low energy conformations of 1,4,7,10-cyclododecatetraenes, which have been calculated bythe molecular mechanics method. These compounds are similar to other 12-membered ring systems, such as cyclic tetrapeptides and 12-crown-4-ethers, and may serve as conformational analogues for these and other structures. Some of the recently synthesized macrocyclic polyethers[1] have aroused considerable interest in several branches of chemistry because they form stable complexes, both in solution and in crystalline form, with salts of alkali and other metals. The ease with which these cyclic polyethers can be synthesized[2] makes them invaluable to those scientists investigating highly structured molecular complexes. Such complexes are, of course, central to nature's enzyme, transport and regulatory systems. Cyclic tetrapeptides are also biologically active, and perform a variety of functions in which their molecular conformation is of great importance.[3]

A.1 GENERATED CONFORMATIONS

The White-Morrow[4] algorithm for location of the GMEC and other low energy conformations of cyclic structures, was initially used to predict the low energy conformations of cyclotetraglycyl[5] (c-Gly 4). Cyclopolyglycyls were used because the polyglycl low energy set can be used as the starting set for any cyclic peptide. This is accomplished by simply replacing hydrogens with the appropriate side chain. After full-minimisation of all starting conformations, 40 low energy conformations resulted.

All 40 of these conformations were converted into 1,4,7,10-cyclododecatetraenes (abbreviated to Tetraenes) via the GUCGS[6]. The nitrogen atoms were replaced by carbon atoms; the NH groups by hydrogens, and the oxygen atoms by hydrogens. Subsequent alteration of atom types and the number of substituents, led to 40 starting conformations for the Tetraenes. Full-minimisation was carried out on all 40 conformations during which, some reached a maximum energy value, and others minimised to the same minimum energy conformation. This left a total of 20 unique low energy conformations for the Tetraenes. There is always the possibility, of there being low energy conformers other than those derived here, since only a selected set of generators was considered. Final V_s values and TAs are recorded in Table 1, while a breakdown of the component energy values of V_s is given in Table 2. The C and T labelling refers to the double bond configuration i.e. CIS or TRANS.

From Table 1, it is readily seen that trans double bonds are, in general, more flexible than cis double bonds. Deviations from planarity of up to 20° in the trans double bonds are not uncommon, while cis double bonds rarely deviate from planarity by 5°, or less. This echoes the situation in the cyclic tetrapeptides and is in accordance with observed structures of polypeptides[7]. All observed structures of

TABLE 1

CONFMn.	V_s kcal./mole	RING TAs°											
				b			b			b			b
$CCCC_1$[a]	7.40	-117	117	0	-117	117	0	-117	117	0	-117	117	0
$CTCT_1$	9.08	-140	75	0	-75	140	-177	140	-75	0	75	-140	177
$CCCT_1$	9.13	120	-69	0	137	-92	2	-92	137	0	-68	120	-174
$CCCT_2$	9.14	-132	58	0	-123	124	0	-108	132	0	-70	-24	-178
$CCCC_2$	9.32	110	-110	0	127	-65	1	-112	112	-1	65	-127	0
$CTCT_2$	10.17	-127	96	0	-46	-71	177	-127	96	0	-46	-71	177
$CTCT_3$	10.47	-126	79	0	-73	-23	176	-23	-73	0	79	-126	175
$CCCC_3$	11.90	-62	141	0	-139	60	-1	62	-141	0	140	-60	1
$CCTT_1$	12.25	-129	51	0	-138	138	0	-51	129	-172	87	-87	172
$CCTT_1$	12.59	-20	-55	-1	-32	126	0	-129	102	177	-58	-29	1
$CCCT_4$	12.86	68	54	0	-138	80	-2	83	80	0	59	38	-176
$CTCT_4$	13.11	-14	-79	0	67	62	-175	14	79	0	-67	-62	175
$CCTT_2$	13.76	-133	141	0	-28	-91	174	-49	-68	173	-130	57	0
$TTTT_1$	15.40	-94	94	-166	94	-94	166	-94	94	-166	94	-94	166
$CTTT_1$	15.63	-142	87	0	-62	-84	174	-53	101	-162	87	-90	169
$CTTT_2$	16.20	96	57	0	-88	141	-169	67	70	-163	82	19	-176
$TTTT_2$	16.59	-77	-75	166	-75	-77	166	-89	99	-167	99	-89	167
$TTTT_3$	16.61	83	83	-166	91	-91	166	-83	-83	166	-91	91	-166
$CCCC_4$	16.62	-9	-86	1	9	86	-1	-9	-86	1	9	86	-1
$TTTT_4$	17.51	72	72	-168	72	72	-168	72	72	-168	72	72	-168

a : subscript refers to the placing of the conformer in the list of increasing V_s, with that particular arrangement for the double bonds.

b : signifies a double bond.

TABLE 2 : all units in kcal./mole

CONFMn	V_1	V_r	V_a	V_w	V_x	V_s
$CCCC_1$	0.28	3.26	3.70	0.16	0.00	7.40
$CTCT_1$	0.21	1.99	1.35	5.49	0.02	9.08
$CCCT_1$	0.27	2.46	2.19	4.15	0.05	9.13
$CCCT_2$	0.27	2.85	2.92	3.10	0.00	9.14
$CCCC_2$	0.33	3.01	3.12	2.85	0.00	9.32
$CTCT_2$	0.26	2.28	2.28	5.31	0.02	10.17
$CTCT_3$	0.30	3.05	1.97	5.08	0.06	10.47
$CCCC_3$	0.29	2.54	3.27	5.76	0.03	11.90
$CCTT_1$	0.32	2.91	4.12	4.61	0.29	12.25
$CCCT_3$	0.37	3.53	4.41	4.26	0.02	12.59
$CCCT_4$	0.30	2.86	2.63	7.03	0.03	12.86
$CTCT_4$	0.33	3.37	2.23	7.10	0.07	13.11
$CCTT_2$	0.39	3.68	4.22	5.32	0.15	13.76
$TTTT_1$	0.24	2.78	3.70	7.06	1.62	15.40
$CTTT_1$	0.31	3.38	3.10	7.97	0.86	15.63
$CTTT_2$	0.37	4.38	2.68	7.98	0.79	16.20
$TTTT_2$	0.24	3.04	2.91	8.86	1.53	16.59
$TTTT_3$	0.24	2.96	3.32	8.46	1.62	16.61
$CCCC_4$	0.42	3.24	9.47	3.47	0.00	16.62
$TTTT_4$	0.25	3.30	1.68	11.05	1.23	17.51

cyclotetrapeptides fall into three basic conformations. One has an all-trans amide configuration, while the other two have a CTCT configuration. The presence of conformations containing cis-amides in a low energy set, is not surprising in view of the strain imposed on an all-trans conformation by ring closure. Even the calculated minimum energy conformation[5] of (c-Gly 4) has considerable Pitzer and Baeyer strain. In contrast, the CTCT conformations, are almost entirely free from strain in the region of the amide groups and this compensates for the presence of the energetically unfavourable cis amides. In the tetrapeptides, the calculated GMEC has large deviations due to out-of-plane bending and non-ideal TAs. The barrier to free rotation is low - approximately 20 kcal $mole^{-1}$ - and this can accommodatethese deviations. However, the barrier to free rotation in the alkenes is approximately 60 kcal $mole^{-1}$, which is too large to accommodate the deviations associated with the trans double bonds. Thus, the calculated GMEC (in this study) is an all cis conformation. Another factor which stabilises the all-trans conformer in the cyclic tetrapeptides, is the presence of hydrogen bonding, this is not present in the alkene case.

Several conformations of Tetraenes have been considered by Dale[8], in an attempt to explain conformational interconversions. However, there is very little quantitative information about the strain energy of those conformations considered.

Dale predicts, for an all-cis arrangement of the double bonds, only four possible conformations which he refers to by the letters A, B, C and D and which differ only in the up-down relationship between the four CH_2 groups. Of these, the one with the up-down alternation, (D), is proposed to be the least favoured as it has two very close transannular interactions. This is supported by the present calculations, in which D corresponds to $CCCC_4$ which is calculated to have the second highest V_s of the 20 calculated conformations. The greatest contribution to the V_s in $CCCC_4$ comes from Baeyer strain, with Pitzer strain and van der Waals interactions contributing

approximately equal amounts.

The A conformer of Dale corresponds to the $CCCC_3$ conformation, and is calculated to have the next highest V_s of the four CCCC conformations. It has very high Pitzer strain with Baeyer strain and van der Waals interactions making less, and approximately equal, energy contributions.

The B conformer corresponds to the $CCCC_2$ conformation. This is predicted to have equal contributions from Pitzer, Baeyer and van der Waals strain. The C conformer of Dale is calculated to be the GMEC of the present study, $CCCC_1$, a "crown" conformation containing high Baeyer and van derWaals strain. All four conformations, $CCCC_1$ - $CCCC_4$, are given in Figures A.1 - A.4, and are annotated with their calculated TAs (°) and steric energies (kcal $mole^{-1}$). The GMEC is highly symmetrical and is preferred to the next calculated conformer by 1.67 kcal $mole^{-1}$. The double bond TAs are all 0°, as expected, while the sp^2-sp^3 angles deviate from their ideal values of $\pm 120^{\circ}$ by only 3°.

The only other conformations of the Tetraenes considered by Dale are those with CTCT arrangements of the double bonds. Cyclic peptides can be considered as belonging to this category, if the conformational barriers for the ring skeleton are lower than the barrier for cis-trans isomerisation of the amide groups. Dale has suggested three likely conformers with CTCT arrangements which will be referred to as A′, B′ and C′. His most favoured arrangement, A′, is a crown-like conformation corresponding to $CTCT_1$ of the present study. This is the type observed for a series of cyclic tetrapeptides[9-10]. The greatest contribution to its V_s arises from Pitzer strain. As mentioned previously, the cyclotetrapeptides fall into three basic conformational groups - one of which is an all-trans arrangement while the other two are CTCT arrangements. It has been suggested[5] that protonation of the TTTT S_4 GMEC of cyclic tetrapeptides leads to a conformational interconversion to CTCT C_I. Conformational

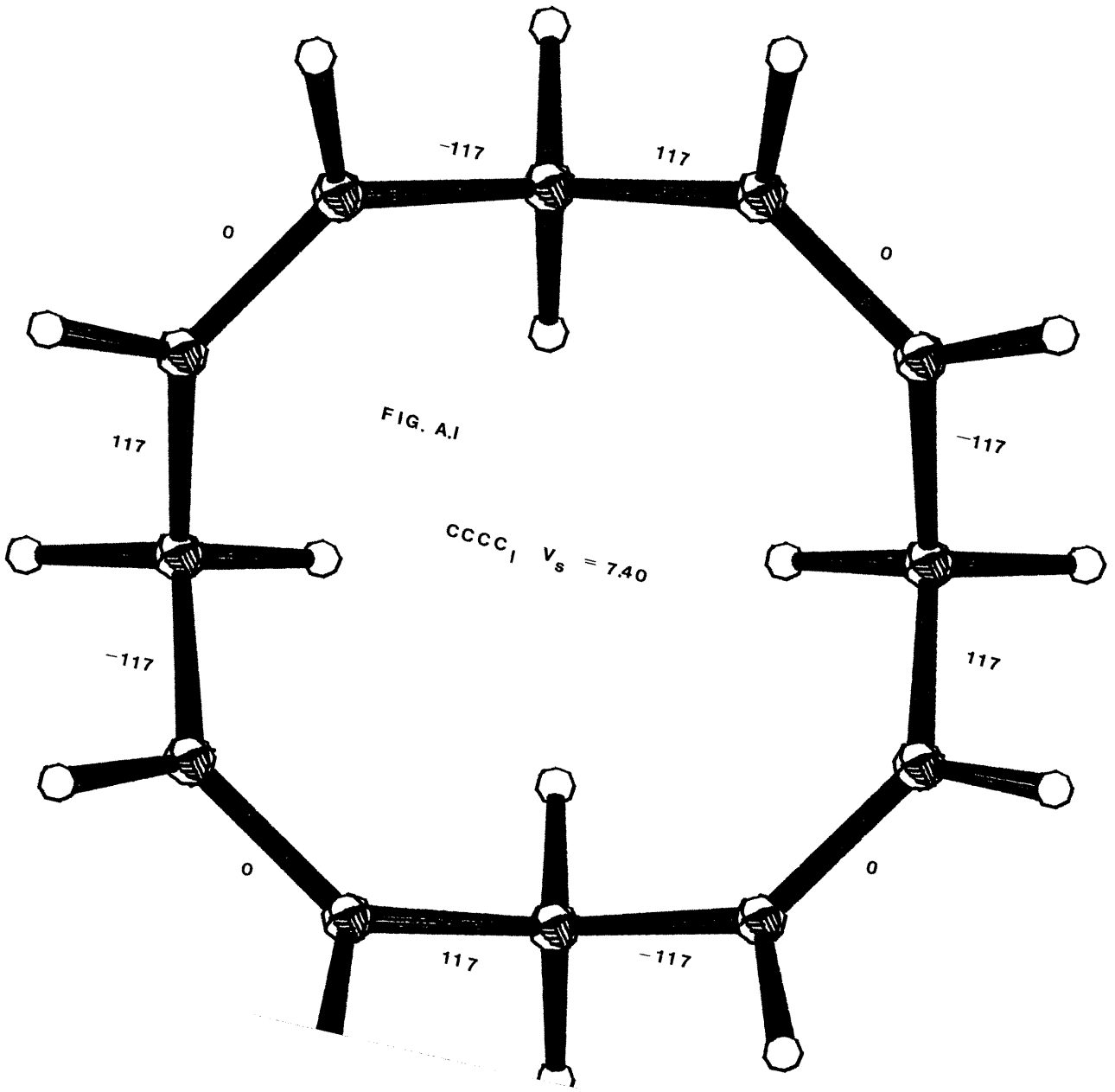


FIG. A.I

$CCCC_I$ $V_s = 7.40$

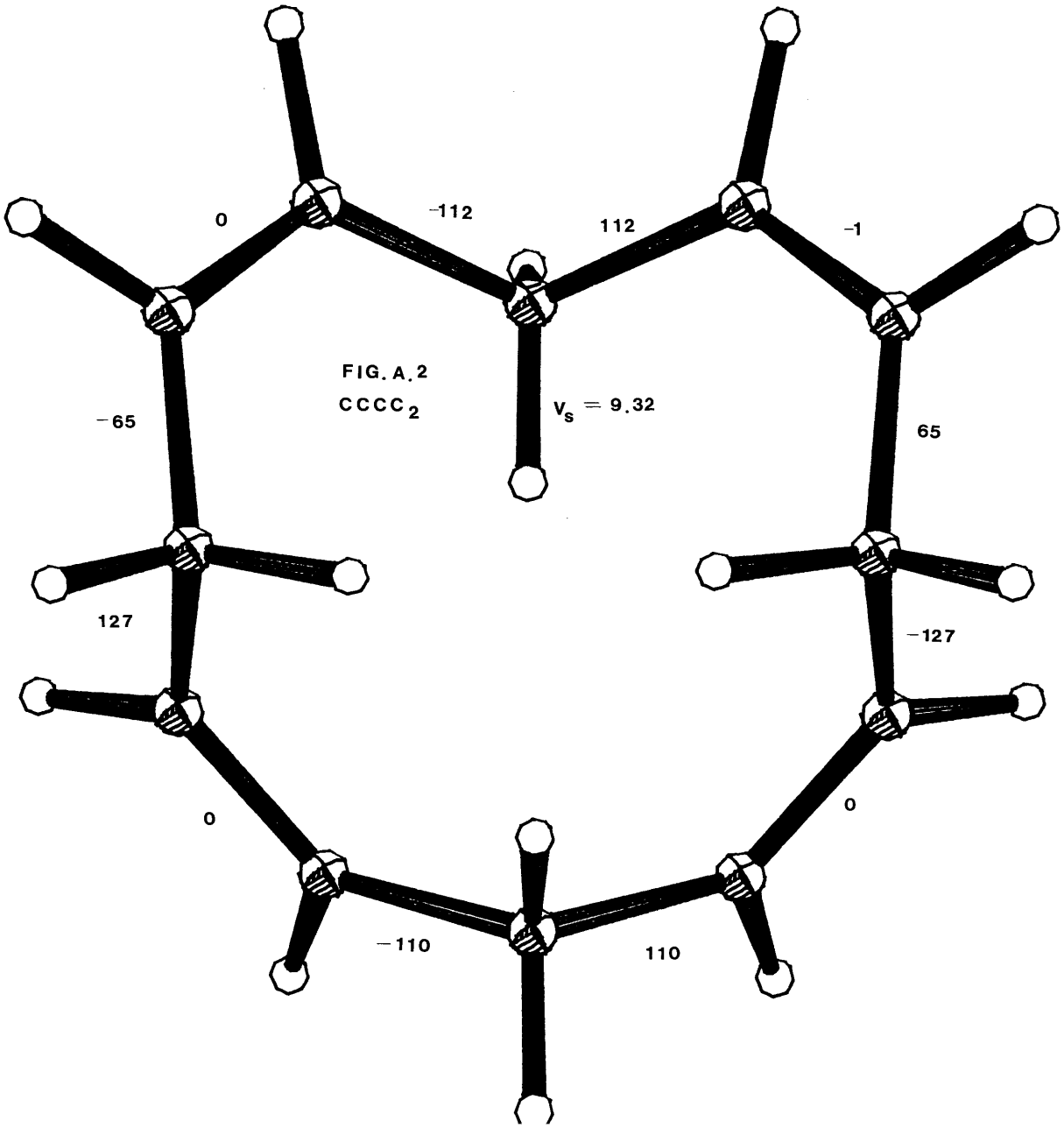


FIG. A.2
$CCCC_2$
$V_s = 9.32$

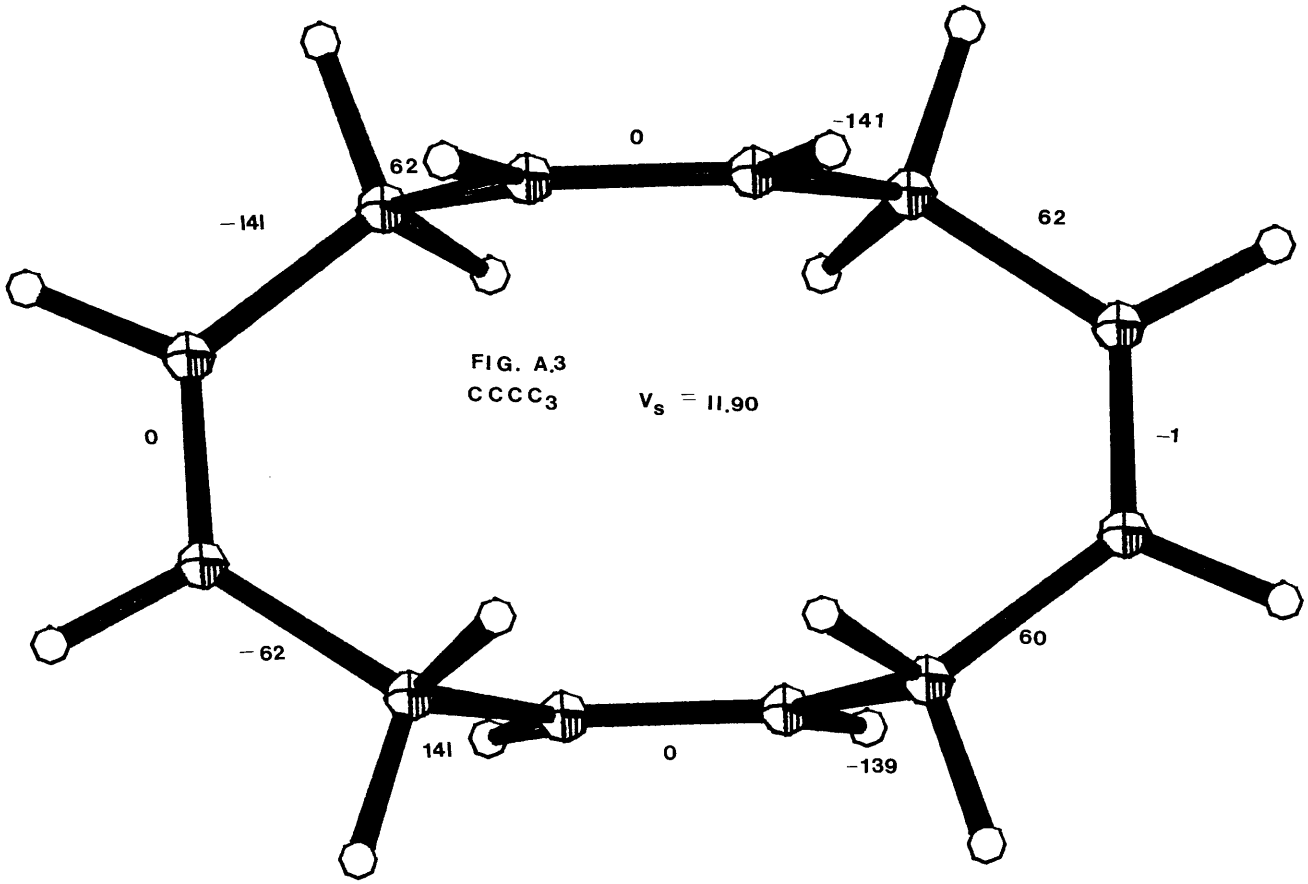


FIG. A.3
$CCCC_3$ $V_s = 11.90$

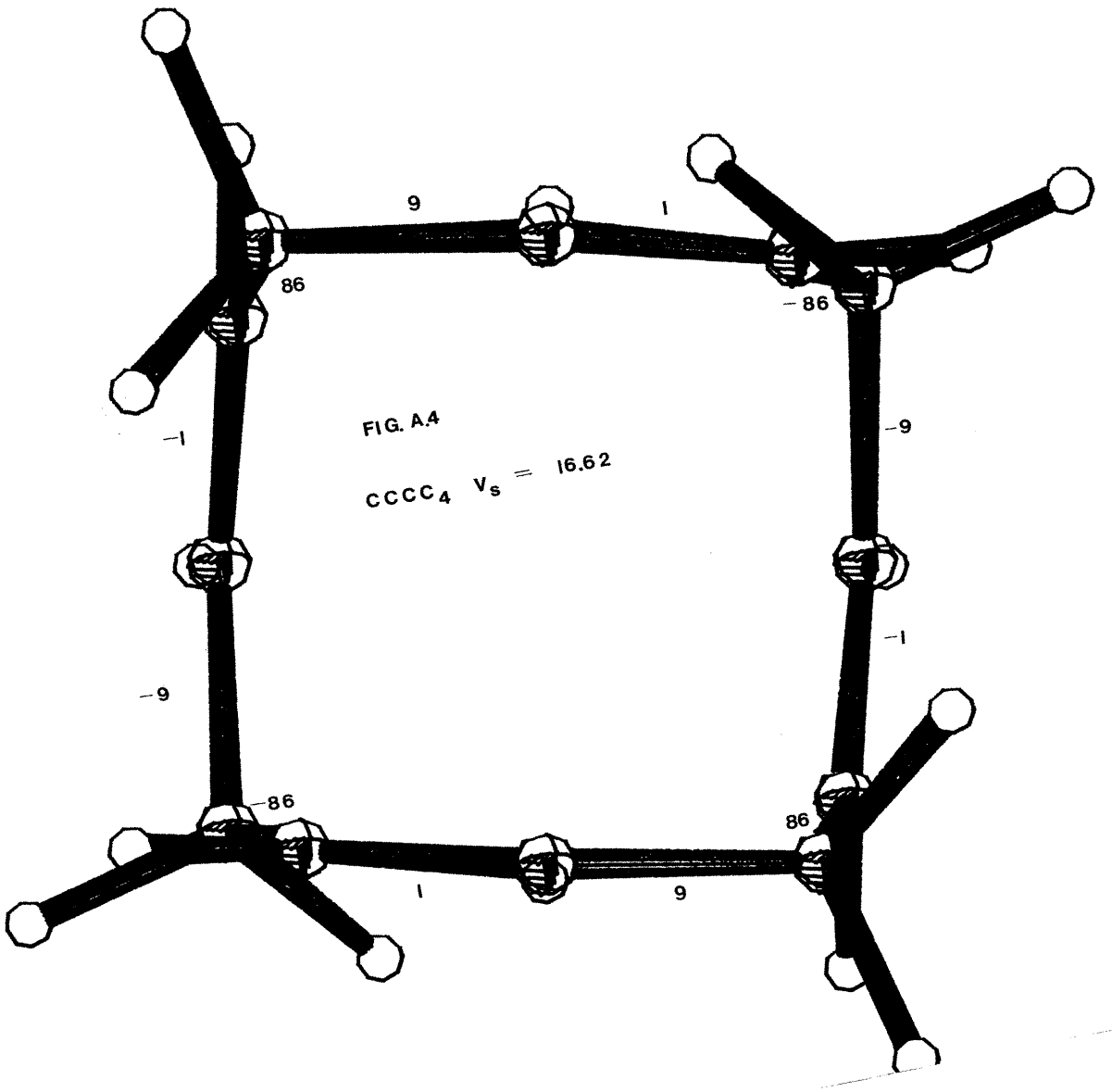


FIG. A.4

$CCCC_4$ $V_s = 16.62$

interconversion from the GMEC, $CCCC_1$, of cyclododecatetraene to the $CTCT_1$ conformation is energetically impossible at room temperature. However, it is interesting to note that the CTCT configuration is predicted in both classes of compounds to be the second lowest energy conformation. This suggests that it is intrinsically stable - there are no transannular interactions and the double bond TAs show only small deviations from ideal values. The B′ conformer does not correspond to any of the conformers calculated here. The C′ corresponds to $CTCT_4$ with most of its strain energy resulting from Pitzer strain. Two other conformations with the CTCT arrangement are predicted to be low energy conformations of the Tetraenes, namely, $CTCT_2$ and $CTCT_3$. All four CTCT conformations are given in Figures A.5 - A.8.

The present study predicts low energy conformations for other arrangements of the double bonds, such as, CCCT, CCTT, CTTT and all-trans arrangements.

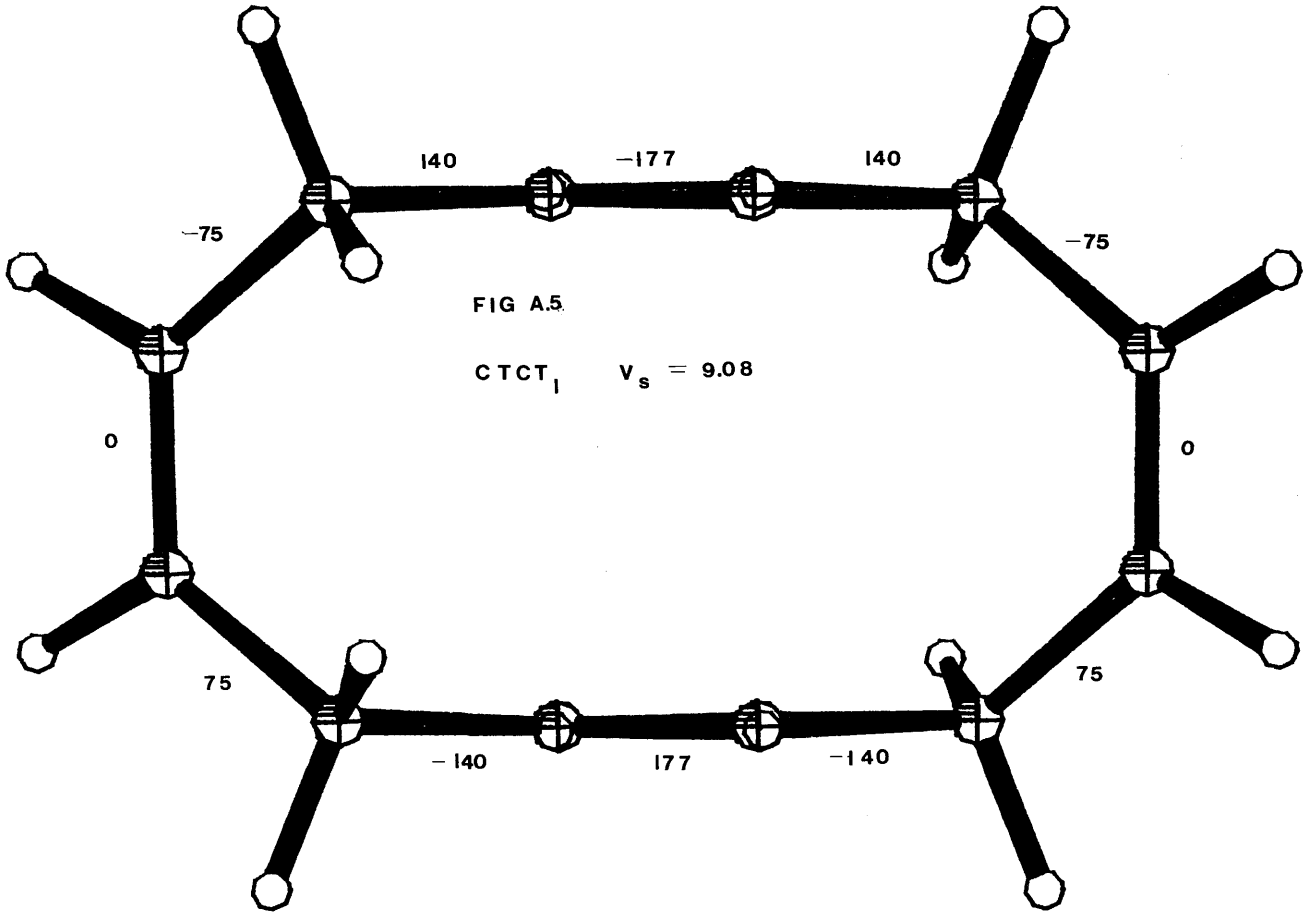


FIG A.5

$CTCT_1$ $V_s = 9.08$

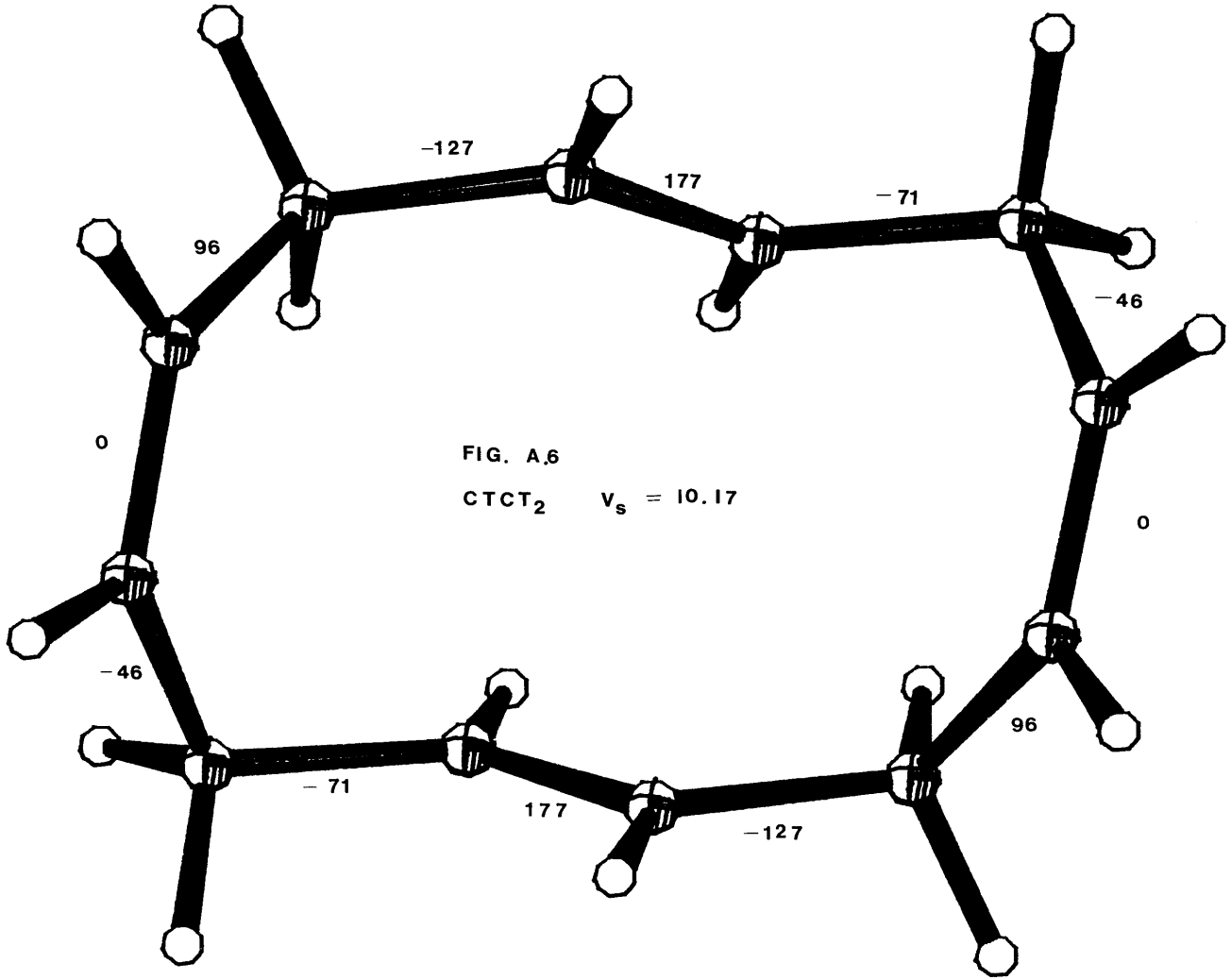


FIG. A.6

$CTCT_2$ $V_s = 10.17$

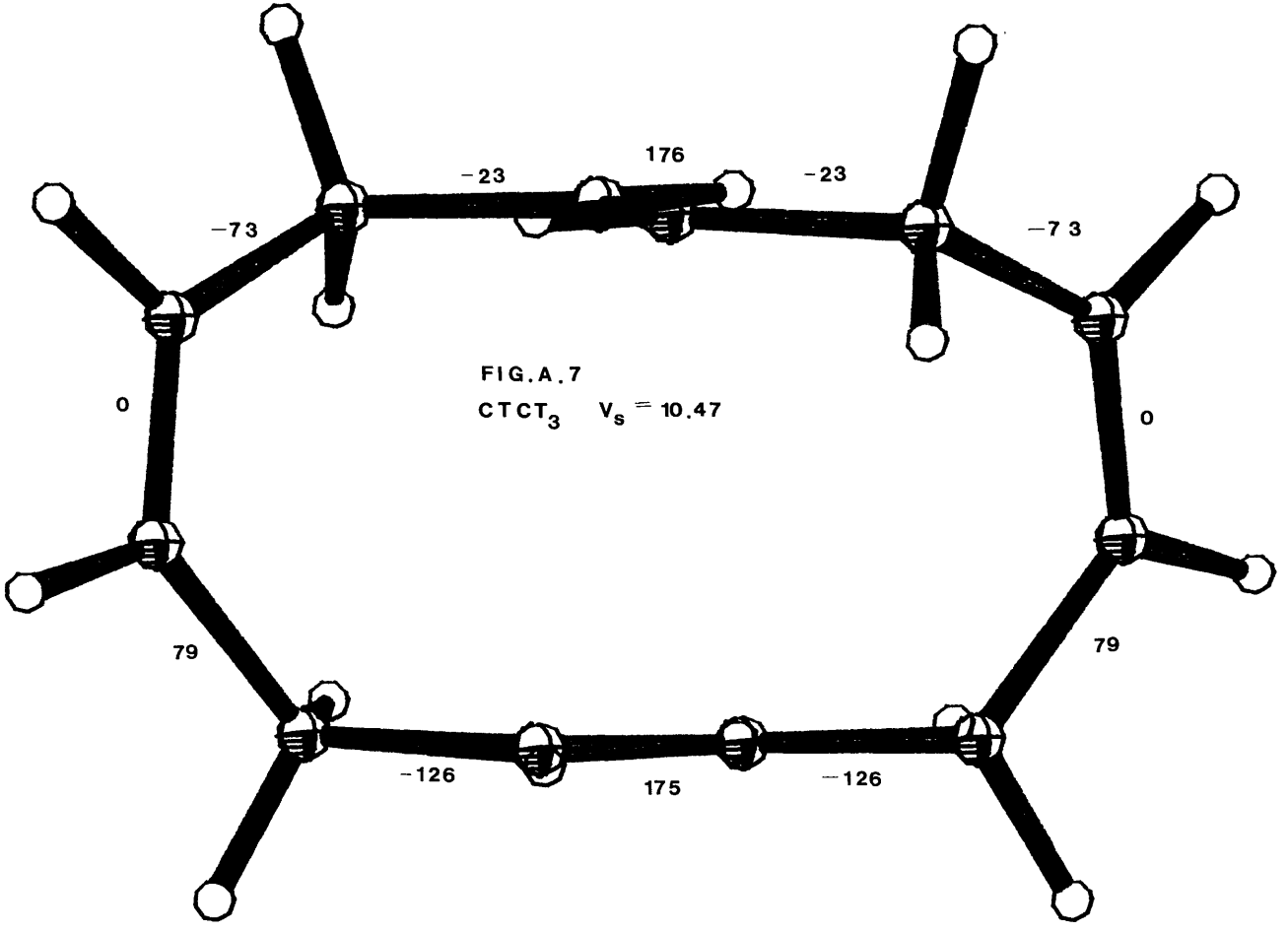


FIG.A.7

$CTCT_3$ $V_s = 10.47$

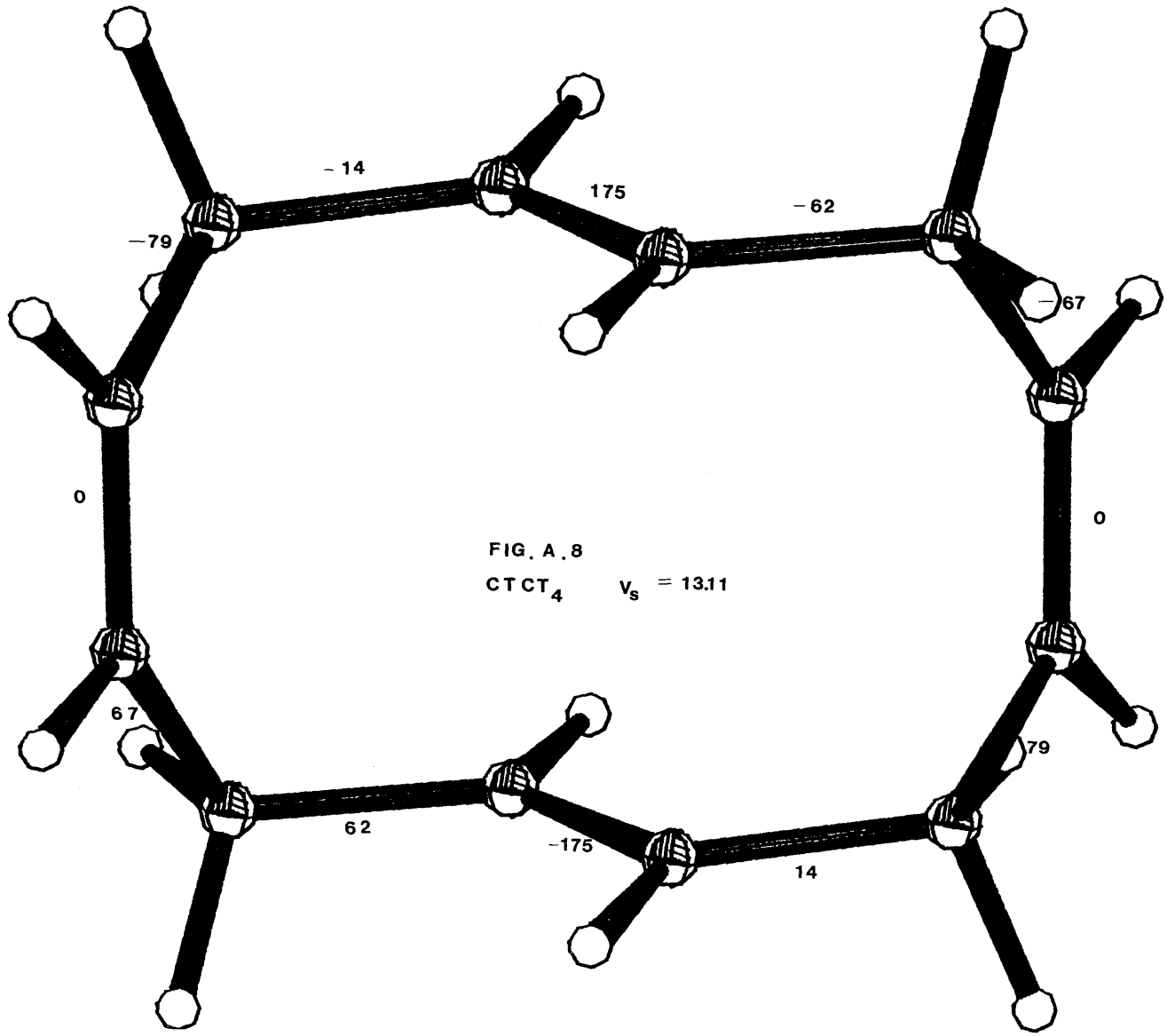


FIG. A.8

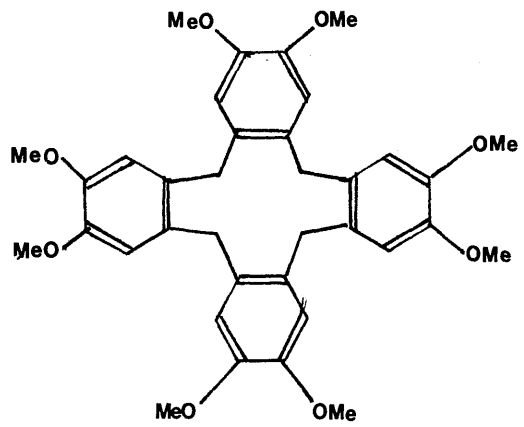
$CTCT_4$ $V_s = 13.11$

A.2 CORRELATION OF OBSERVED AND CALCULATED CONFORMATIONS

(a) The all cis "crown" GMEC.

The Tetraene itself is not known, but the corresponding tetrakis (4,5-dimethoxybenzo) derivative - cyclotetraveratrylene (I) - has been studied by NMR[11] and is shown to be quite flexible at temperatures between 229 and 319 K.

(I)



The most stable form is the "sofa" conformation of type $CCCC_3$ with full exchange occurring over a barrier of 13 kcal $mole^{-1}$. It has been proposed that the mechanism is a successive rotation of the four CH_2 groups via the crown conformation of type $CCCC_1$. White and Gesner[11] suggest that the crown conformation relieves a serious steric interaction of aromatic protons on adjacent rings.

No other evidence has been forthcoming on the preferred conformation of 1,4,7,10-cyclododecatetraene and it is unfortunate that the evidence mentioned refers to a derivative rather than the cyclotetraene itself.

(b) CTCT Conformers.

This configurational sequence is observed in a number of peptides[9-10] and depsipeptides[13]. $CTCT_1$ bears a strong resemblence to a number of these peptides and depsipeptides as

indicated by a comparison of their TAs in Table 3. Also included in this list are the TAs of a Tentoxin derivative[14].

(c) All-trans Conformers.

The TTTT conformations of the Tetraenes are of higher strain energy than most of the other conformers, yet, comparable conformations are observed for crown ethers, tetrapeptides and cyclododecane.

A conformation with C_4 symmetry was inferred from the results of an x-ray analysis of cyclododecane[15] in which the crystal structure is disordered. A similar conformation is adopted by azocyclododecane[16], 1,1-dihydroperoxycyclododecane[17] and various hydrated complexes of 1,4,7,10-tetraoxacyclododecanes[18-19]. These compare favourably with that of $TTTT_4$ calculated for cyclododecatetraene and a comparison of the TAs is given in Table 4.

The $TTTT_4$ conformer is calculated to have the greatest V_s of the 20 low energy conformers calculated here. The bulk of its strain energy is due to torsional strain around the double bonds as a result of deviations of these TAs from ideal values. Non-planarity also results from out-of-plane bending at the trigonal atoms. The preferred TA for a single bond next to a double bond is 120° with an hydrogen atom of a CH_2 group eclipsing a double bond. In $TTTT_4$, we are very far removed from this ideal situation.

For 1,4,7,10-tetraoxacyclododecane (12-crown-4), the expected quadrangular conformation of C_4 symmetry is found. It is comparable to the most stable conformation of cyclododecane. It contains ($\pm$gauche, $\pm$gauche, anti) units which are referred to as "genuine" corners[21]. Uncomplexed or incompletely complexed crown ethers, however, adopt unusual conformations which are not encountered in cycloalkanes. These latter crown ethers contain ($\pm$gauche,$\mp$gauche, anti) units which are termed "pseudo" corners.

TABLE 3

Ring TAs (°) for :

	a	b	c	d	e	f	g	h
	-140	-121	-125	-121	-130	-129	-150	-120
	75	66	71	61	63	70	51	60
*	0	6	-7	2	1	-6	19	0
	-75	-94	-85	-91	-91	-83	-106	-90
	140	170	166	177	166	165	142	160
*	-177	-171	-173	-169	-170	-175	-178	180
	140	121	125	124	128	124	150	130
	-75	-65	-71	-65	-67	-68	-51	-85
*	0	-5	7	-7	-5	3	-19	0
	75	94	85	94	91	85	51	60
	-140	-170	-166	-165	-159	-162	-142	-150
*	177	171	173	175	-179	175	178	180

* signifies a double bond.

a = calculated $CTCT_1$

b = c-Sar_4[9]

c = c-$(GlySar)_2$[12]

d = c-Gly-$(Sar)_3$[12]

e = c-D-Ala-$(Sar)_3$[12]

f = c-L-Ala-$(Sar)_3$[12]

g = c-D-MeVal-L-HyIv-L-MeVal-D-HyIv[13]

h = D-MeAla(1)-Tentoxin(L1)[14]

TABLE 4

Ring TAs (°) for :

	a	b	c	d	e	f
	72	68	64	78	60	68
	72	69	71	59	79	69
*	-168	-161	-154	-165	-165	-158
	72	70	66	81	59	69
	72	67	71	60	81	66
*	-168	-155	-169	-165	-163	-164
	72	67	67	79	59	69
	72	70	69	56	80	69
*	-168	-163	-155	-164	-166	-157
	72	69	70	83	59	69
	72	68	68	59	80	68
*	-168	-155	-168	-164	-162	-160

* signifies a double bond.

a = calculated $TTTT_4$.

b = Cyclododecane[15]

c = Azacyclododecane[16]

d)[18] e)[19] = hydrated complexes of tetraoxacyclododecane.

f = 1,1-digyroperoxycyclododecane[17]

These are characterised by close 1,5 CH....O interactions. A centrosymmetric biangular [66] conformation with two pseudo corners is found in a crystalline complex[22] with $MgCl_2$ and also for the crystalline crown ether[23] itself. These correspond to the calculated $TTTT_3$ conformer of the Tetraenes - as shown by a comparison of their TAs in Table 5. Included in this table are the recorded TAs for a depsipeptide crystal structure[24] which also has this conformation.

The calculated all-trans conformer of the Tetraenes with lowest V_s, $TTTT_1$, has a conformation comparable to that found in dihydrochlamydocin[25], (II), as shown by their TAs in Table 6.

(II)

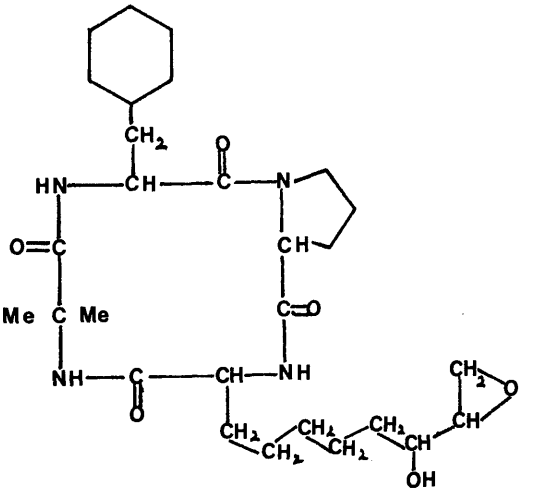


TABLE 5

Ring TAs (°) for :

	a	b	c	d
	83	71	75	76
	83	91	85	49
*	-166	-117	-140	-163
	91	83	75	125
	-91	-98	-103	-94
*	166	147	174	-168
	-83	-71	-75	-76
	-83	-91	-85	-49
*	166	117	140	163
	-91	-83	-75	-125
	91	98	103	94
*	-166	-147	-174	168

* signifies a double bond.

a = calculated $TTTT_3$

b = 1:1 hexahydrate complex of $MgCl_2$ with 1,4,7,10-tetraoxacyclododecane[22].

c = 1,4,7,10-tetraoxacyclododecane[23].

d = c-L-MeVal-L-HyIv-D-MeVal-D-HyIv.[24]

TABLE 6

Ring TAs (°) for :

a	b	
-94	-105	
94	94	
-166	162	*
94	83	
-94	-73	
166	-166	*
-94	-105	
94	105	
-166	156	*
94	72	
-94	-64	
166	-164	*

* signifies a double bond.

a = calculated $TTTT_1$

b = Dihydrchlamydocin[25].

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APPENDIX B

WHITE-BOVILL FORCE FIELD PARAMETERS

Atom key : 1 = H, 2 = $C(sp^2)$, 3 = $C(sp^3)$;
Force constants are in kcal mol^{-1} $Å^{-2}$ or in kcal mol^{-1} K^{-2};
energies are in kcal mol^{-1}.

Bond Stretching

Atoms	$1/2k_l$	l_0
1-2	346.0	1.089
1-3	331.2	1.100
2-2	670.0	1.335
2-3	319.5	1.501
3-3	316.8	1.535

Van der Waals

Atoms	r_1^*	r_2^*	e
1....1	3.10	0.0	0.0160
1....2	3.53	0.0	0.0330
1....3	3.35	0.0	0.0299
2....2	4.00	0.0	0.0760
2....3	3.60	0.0	0.0800
3....3	3.85	0.0	0.1200

Angle Bending

Atoms	$1/2k_a$	k'_a	$^*a^1_0$	a^2_0	a^3_0	a^4_0
1-2-1	0.0055	0.0096	118.6			
1-2-2	0.0060	0.0	121.7	120.4		
1-2-3	0.0060	0.0		117.5		
2-2-3	0.0120	0.0096		122.3	121.0	
3-2-3	0.0233	0.0096			116.4	
1-3-1	0.0072	0.0096	108.2	109.1		
1-3-2	0.0088	0.0096	110.5	110.0	110.2	
1-3-3	0.0088	0.0096	109.0	109.2	109.2	

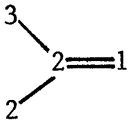
2-3-2	0.0090	0.0096	111.0	110.1	109.5
2-3-3	0.0090	0.0096	110.4	110.1	109.5
3-3-3	0.0120	0.0096	110.4	110.1	109.5

* Superscript indicates the degree of substitution at the central atom.

Torsion

ATOMS	$1/2k_w$	s	n
1-2-2-1	6.2500	-1	2
1-2-2-3	6.2500	-1	2
3-2-2-3	6.2500	-1	2
1-2-3-1	0.1367	1	3
1-2-3-2	0.1367	1	3
1-2-3-3	0.1367	1	3
2-2-3-1	0.0629	-1	3
2-2-3-2	0.0629	-1	3
2-2-3-3	0.0629	-1	3
3-2-3-1	0.0629	1	3
3-2-3-2	0.0629	1	3
3-2-3-3	0.0629	1	3
1-3-3-1	0.1100	1	3
1-3-3-2	0.1100	1	3
1-3-3-3	0.1100	1	3
2-3-3-2	0.0200	1	3
2-3-3-3	0.0629	1	3
3-3-3-3	0.0629	1	3

Out-of-plane Bending

	$1/2k_x$
	0.0020

Extra parameters for ketonic function

Atom key : as above with 4 = O(sp^2)

Bond Stretching

Atom	$1/2k_1$	l_0
2-4	685.0	1.212

Van der Waals

Atom	r^*_1	r^*_2	e
1....4	3.60	0.0	0.0400
2....4	3.80	0.0	0.0200
3....4	3.60	0.0	0.0700
4....4	4.00	0.0	0.0850

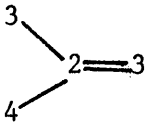
Angle Bending

Atoms	$1/2k_a$	k'_a	a^1_0	a^2_0	a^3_0	a^4_0
1-2-4	0.0085	0.0	122.0	121.5		
3-2-4	0.0125	0.0096		121.0	119.0	

Torsion

Atoms	$1/2k_w$	s	n
1-3-2-4	0.0400	-1	3
3-3-2-4	0.0600	-1	3
2-3-2-4	0.0600	-1	3

Out-of-plane Bending

	$1/2k_x$
	0.0025

Extra parameters for conjugation

Atom key : as above with 4 = $C(sp^2)$ - for both carbons of the exocyclic double bond.

Bond Stretching

Atoms	$1/2k_1$	l_0
1-4	346.0	1.089
2-4	319.5	1.501
4-4	670.0	1.335

Van der Waals

Atom	r^*_1	r^*_2	e
1....4	3.53	0.0	0.0330
2....4	4.00	0.0	0.0760
3....4	3.60	0.0	0.0800
4....4	4.00	0.0	0.0760

Angle Bending

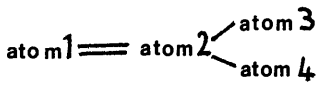
Atoms	$1/2k_a$	k'_a	a^1_0	a^2_0	a^3_0	a^4_0
1-4-1	0.0055	0.0096	118.6			

1-4-4	0.0060	0.0	121.7	120.4	
1-2-4	0.0060	0.0	121.7	118.9	
2-2-4	0.0120	0.0096		122.3	121.0
2-4-2	0.0233	0.0096			116.4
2-4-4	0.0120	0.0096		122.3	121.0
3-2-4	0.0233	0.0096			116.4

Torsion

Atoms	$1/2k_w$	s	n
1-2-2-4	6.25	-1.0	2
3-2-2-4	6.25	-1.0	2
1-2-4-2	0.625	-1.0	2
1-2-4-4	0.625	-1.0	2
1-4-4-2	6.25	-1.0	2
2-2-4-2	0.625	-1.0	2
2-2-4-4	0.625	-1.0	2
3-2-4-2	0.625	-1.0	2
3-2-4-4	0.625	-1.0	2
4-2-3-1	0.0629	1.0	3

Out-of-Plane



Atom 1	Atom 2	Atom 3	Atom 4	$1/2k_x$
2	2	1	3	0.0035
2	2	3	1	0.0035
2	2	3	3	0.0035
2	2	1	4	0.0035
2	2	4	4	0.0035
4	1	4	1	0.0035

APPENDIX C

STRUCTURE FACTORS (OBSERVED AND CALCULATED).

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	0	0	111	131	10	2	0	4	-4	11	5	0	6	6	-3	1	1	20	-21	6	2	1	13	-13
2	0	0	4	-4	11	2	0	6	-5	0	6	0	12	12	-2	1	1	5	-5	7	2	1	2	-2
3	0	0	103	-110	12	2	0	6	6	1	6	0	7	7	-1	1	1	58	-60	8	2	1	14	13
4	0	0	33	32	13	2	0	2	-2	2	6	0	6	-6	0	1	1	50	53	9	2	1	12	-13
5	0	0	49	-48	14	2	0	4	-4	3	6	0	4	2	1	1	1	17	17	10	2	1	2	2
6	0	0	18	18	15	2	0	1	-2	4	6	0	4	4	2	1	1	70	70	11	2	1	6	-6
7	0	0	13	12	1	3	0	6	6	5	6	0	8	7	3	1	1	33	36	13	2	1	3	-4
8	0	0	5	-4	2	3	0	22	20	6	6	0	7	7	4	1	1	5	5	14	2	1	4	4
9	0	0	5	4	3	3	0	9	-8	7	6	0	12	12	5	1	1	18	-18	-14	3	1	10	10
10	0	0	4	-3	4	3	0	27	-28	8	6	0	4	4	6	1	1	23	-22	-11	3	1	2	2
11	0	0	9	10	5	3	0	32	-33	9	6	0	2	1	7	1	1	14	-14	-10	3	1	20	20
12	0	0	12	13	6	3	0	14	15	10	6	0	2	-2	8	1	1	6	-6	-9	3	1	2	-2
15	0	0	2	2	7	3	0	22	22	1	7	0	5	5	9	1	1	4	-4	-8	3	1	21	20
1	1	0	40	43	8	3	0	11	10	2	7	0	6	6	10	1	1	2	-2	-7	3	1	19	18
2	1	0	72	-74	9	3	0	19	-19	3	7	0	3	3	11	1	1	3	-4	-6	3	1	5	-5
3	1	0	62	61	10	3	0	6	6	4	7	0	3	-3	12	1	1	8	8	-5	3	1	3	-4
4	1	0	7	-6	11	3	0	3	3	5	7	0	7	-7	13	1	1	2	-2	-4	3	1	7	-7
5	1	0	24	-24	12	3	0	8	8	6	7	0	6	-5	14	1	1	2	-2	-3	3	1	10	11
6	1	0	63	-60	14	3	0	4	4	7	7	0	4	-4	-13	2	1	5	5	-2	3	1	4	3
7	1	0	21	21	0	4	0	36	35	8	7	0	2	-2	-11	2	1	3	-3	-1	3	1	9	8
8	1	0	9	-8	2	4	0	14	-14	0	8	0	3	-3	-10	2	1	12	-12	0	3	1	39	-41
9	1	0	4	4	3	4	0	23	-21	1	8	0	5	-5	-9	2	1	6	-6	1	3	1	11	-12
11	1	0	2	2	4	4	0	2	1	2	8	0	4	-4	-8	2	1	12	11	2	3	1	45	47
12	1	0	1	-1	5	4	0	9	-9	5	8	0	4	-4	-7	2	1	33	-33	3	3	1	7	8
13	1	0	2	-2	6	4	0	4	3	6	8	0	3	-4	-6	2	1	13	-13	4	3	1	11	-10
15	1	0	3	3	7	4	0	2	-2	-15	1	1	2	2	-5	2	1	28	-28	5	3	1	16	-15
0	2	0	14	-13	9	4	0	19	-19	-14	1	1	2	2	-4	2	1	7	-8	6	3	1	22	23
1	2	0	16	16	10	4	0	7	-8	-13	1	1	3	-3	-3	2	1	12	12	7	3	1	3	-3
2	2	0	97	-96	11	4	0	4	-3	-12	1	1	4	-4	-2	2	1	109	112	8	3	1	8	7
3	2	0	33	-35	3	5	0	4	-4	-11	1	1	3	-3	-1	2	1	83	84	9	3	1	6	7
4	2	0	20	-20	4	5	0	10	-9	-9	1	1	5	5	0	2	1	35	-36	10	3	1	2	2
5	2	0	25	-25	5	5	0	9	-10	-8	1	1	7	-7	1	2	1	75	-80	11	3	1	3	-3
6	2	0	8	-8	6	5	0	3	-2	-7	1	1	22	-21	2	2	1	64	-69	13	3	1	2	1
7	2	0	22	22	7	5	0	5	5	-6	1	1	11	-12	3	2	1	7	-6	14	3	1	2	2
8	2	0	24	24	8	5	0	4	4	-5	1	1	30	-31	4	2	1	8	-7	-13	4	1	4	3
9	2	0	10	-9	9	5	0	3	3	-4	1	1	33	32	5	2	1	30	-29	-12	4	1	2	1

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-11	4	1	7	-7	2	5	1	6	5	0	7	1	9	-8	11	0	2	6	-7	-10	2	2	4	-4
-10	4	1	3	-4	3	5	1	4	-4	1	7	1	8	-8	13	0	2	9	9	-9	2	2	7	7
-9	4	1	3	-3	4	5	1	6	-6	2	7	1	6	-6	14	0	2	6	-6	-8	2	2	2	1
-8	4	1	7	-7	5	5	1	11	11	3	7	1	2	-3	15	0	2	1	1	-7	2	2	19	19
-7	4	1	6	6	7	5	1	12	-12	6	7	1	9	9	-15	1	2	2	-2	-6	2	2	6	-7
-6	4	1	5	-6	8	5	1	6	-6	7	7	1	10	10	-14	1	2	2	3	-5	2	2	29	29
-4	4	1	5	5	9	5	1	8	-8	8	7	1	4	4	-13	1	2	2	1	-4	2	2	12	12
-3	4	1	6	-5	-11	6	1	4	-4	9	7	1	3	3	-12	1	2	6	6	-3	2	2	22	22
-2	4	1	8	-8	-10	6	1	5	-5	-7	8	1	3	3	-11	1	2	8	-8	-2	2	2	116	-121
-1	4	1	6	-5	-8	6	1	7	7	1	8	1	2	-2	-9	1	2	19	-19	-1	2	2	187	-188
0	4	1	17	18	-7	6	1	8	8	2	8	1	4	-4	-8	1	2	9	9	0	2	2	55	-58
1	4	1	2	-1	-6	6	1	6	6	6	8	1	2	-2	-7	1	2	11	10	1	2	2	42	48
2	4	1	1	1	-5	6	1	6	-7	-15	0	2	2	2	-5	1	2	21	-21	2	2	2	64	68
3	4	1	12	-12	-3	6	1	9	9	-14	0	2	4	-4	-4	1	2	34	-34	3	2	2	10	10
4	4	1	5	5	-2	6	1	7	7	-12	0	2	7	7	-3	1	2	25	24	4	2	2	20	17
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13	4	1	2	3	6	6	1	6	6	-3	0	2	132	-146	5	1	2	46	-45	-13	3	2	2	1
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-8	5	1	22	-22	11	6	1	2	2	2	0	2	37	43	10	1	2	3	-4	-7	3	2	30	-29
-7	5	1	6	-6	-8	7	1	3	2	3	0	2	23	24	11	1	2	4	-4	-6	3	2	10	-10
-6	5	1	4	3	-7	7	1	4	4	4	0	2	31	31	12	1	2	11	-12	-5	3	2	3	-2
-4	5	1	4	4	-6	7	1	5	5	5	0	2	5	-5	13	1	2	6	-6	-4	3	2	15	15
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H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	3	2	3	-2	-9	5	2	2	-2	-1	7	2	5	-5	2	1	3	72	-75	11	2	3	7	6
3	3	2	15	-16	-8	5	2	7	-6	1	7	2	5	-5	3	1	3	23	25	13	2	3	4	-4
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6	3	2	9	9	-5	5	2	5	-5	4	7	2	2	2	6	1	3	8	-8	-8	3	3	2	-2
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4	4	2	3	-3	5	6	2	4	3	-7	1	3	15	-14	1	2	3	46	49	-10	4	3	3	-3
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7	4	2	8	-8	9	6	2	4	4	-5	1	3	5	5	3	2	3	25	-26	-8	4	3	4	-4
8	4	2	7	7	10	6	2	1	1	-4	1	3	79	-79	4	2	3	14	-15	-7	4	3	10	-9
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13	4	2	5	4	-4	7	2	6	6	-1	1	3	35	36	7	2	3	18	18	-4	4	3	30	-31
-12	5	2	6	6	-3	7	2	2	2	0	1	3	62	-63	8	2	3	15	14	-3	4	3	61	-58
-11	5	2	3	3	-2	7	2	4	-4	1	1	3	39	-41	9	2	3	6	-6	-2	4	3	33	-34

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
-1	4	3	8	-8	0	6	3	10	10	-7	0	4	3	2	2	1	4	79	83	12	2	4	6	-6
0	4	3	29	29	1	6	3	8	7	-6	0	4	5	5	3	1	4	28	29	13	2	4	2	2
1	4	3	16	17	3	6	3	5	-5	-5	0	4	42	44	4	1	4	41	-40	14	2	4	8	-8
3	4	3	25	-26	4	6	3	9	9	-4	0	4	18	-18	5	1	4	43	-45	-13	3	4	4	-4
4	4	3	20	-20	5	6	3	8	8	-3	0	4	79	83	6	1	4	11	-10	-10	3	4	24	23
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6	4	3	13	13	8	6	3	6	-6	-1	0	4	34	39	8	1	4	5	5	-8	3	4	6	6
7	4	3	9	-9	9	6	3	3	-3	0	0	4	18	18	10	1	4	2	-2	-7	3	4	3	-3
13	4	3	5	-5	10	6	3	3	-4	1	0	4	64	74	11	1	4	7	-7	-5	3	4	27	-25
-12	5	3	2	-2	11	6	3	4	-4	2	0	4	23	-24	12	1	4	2	1	-4	3	4	26	-25
-11	5	3	2	-2	-9	7	3	4	4	3	0	4	49	54	13	1	4	7	-8	-3	3	4	12	-12
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END OF LISTING OF FILE :GACV68.ZERUM(1,*,1).SHELOUT(1) FOR USER GACV68 AT 1980/09/24__20:24:59
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